Studies of amidines and their complexes with the nickel elements

James Barker

STUDIES OF AMIDINES AND THEIR COMPLEXES WITH THE NICKEL ELEMENTS

by

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"The University is a mecca to which students come with something less than perfect faith. It is important that students bring a certain ragamuffin, barefoot irreverance to their studies; they are not here to worship what is known, but to question it."

Prof. J. BRONOWSKI,

"The Ascent of Man", 1973.

To my wife Linda

and my Parents

DECLARATION

The work described in this thesis was carried out in the University of Durham between October 1981 and September 1984. It has not been submitted, either wholly or in part, for a degree in this or any other University and is the original work of the author except where acknowledged by reference.

JAMES BARKER: STUDIES OF AMIDINES AND THEIR COMPLEXES WITH THE NICKEL ELEMENT

ABSTRACT

Amidines [RNC(R′)NR, I] and their complexes of the nickel group metals have been studied. Accurate mass spectrometry applied to (R′=H, R=Ph; R′=CH_3, R=Ph; R′=Ph=R) have given detailed fragmentation patterns which form the basis for the interpretation of related amidines. Differences in skeletal fragmentation patterns were noted between formamidines and acetamidines/benzamidines, ^{1}H, ^{13}C and ^{19}F n.m.r. and mass spectroscopy of lithioamidines indicate a bidentate symmetrically bonded amidine.

The reactions of amidines [RN(X)C(R′)NR] X=H, Li) with compounds of the nickel group metals, results in a wide variety of complexes; their nature depending on the amidine substituents, the metal and the synthetic route used. Complexes with N,N′chelate, *ortho*-metallated, and bridging groups were prepared and characterised together with complexes containing new N,N′chelate and bridging groups, resulting from nucleophilic attack of an amidine at a coordinated nitrile.

The reactions of $M(PhCN)_2Cl_2$ (M=Pd, Pt) and anhydrous $NiCl_2$ with lithioamidines result in yellow $Pt(Am)_2$, where Am = RNC(R′)NR, red $Pd_2(Am)_4$ and dark green $Ni_2(Am)_4$ complexes. The platinum complexes are monomeric for the acetamidine (R′=CH_3), and benzamidine (R′=C_6H_5) ligands, though for palladium the benzamidine complexes are dimeric. The nickel complexes are dimeric for the acetamidine, and benzamidine ligands. Spectroscopic studies indicate that the amidino-groups adopt a carboxylate type mode of bonding through the two nitrogen atoms, and the structure of one of

the complexes, bis, N,N´diphenylbenzamidine-platinum(II) has been characterised by X-ray crystallography. The structure showed a monomeric PtN_4 square planar unit. N.m.r. (^{19}F and ^{13}C) studies have indicated fluxionality when M=Pd, R´=C_6H_5, R=C_6H_4-F-*p*. With K_2MCl_4(M=Pd, Pt) and $NiCl_2$, N,N´diarylamidines form polymeric *ortho*-metallated complexes, N,N´diarylformamidines and acetamidines form six-membered rings, benzamidines five-membered.

Treatment of $Pt(PhCN)_2Cl_2$ with $HN(Li)(C_6H_5)NH$ results in nucleophilic attack at the nitrile and formation of $Pt[HNC(C_6H_5)NC(C_6H_5)NH]_2$. A similar reaction occurred with $Pd(PhCN)_2Cl_2$ and $HNLiC(C_4H_9)NH$.

ACKNOWLEDGEMENTS

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I would also like to thank my friends, Smog, John, Clive, Alan, Jim, Dave, Nigel and Bob for discussions and encouragement throughout the project.

Finally, thanks to "our lass" Linda, for her support and encouragement and to Mrs. Marion Wilson for typing this thesis and deciphering my hieroglyphics.

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Durham 1985.

MEMORANDUM

The author would like to thank Dr. R.O. Gould (University of Edinburgh) for determining the X-ray crystal structure of $Pt[PhNC(Ph)NPh]_2$ and Mr. S.A. Johnson (University of Durham) for the E.S.C.A. data contained in this thesis.

NOTATION

A shorthand notation has been used to describe the amidines used in the following chapters. The amidines are listed below with their abbreviations.

DPFAH	N,N´diphenylformamidine
DPAAH	N,N´diphenylacetamidine
DPTAAH	N,N´di-*p*-tolylacetamidine
DPBAH	N,N´diphenylbenzamidine
DMBAH	N,N´dimethylbenzamidine
DPTBAH	N,N´di-*p*-tolylbenzamidine
DPFPBAH	N,N´di-*p*-fluorophenylbenzamidine
DPIPBAH	N,N´di-*p*-isopropylphenylbenzamidine

CONTENTS

CHAPTER ONE

A STUDY OF PSEUDO-ALLYL CHEMISTRY, WITH PARTICULAR REFERENCE TO THE AMIDINE LIGAND

1.1 Introduction

Though large numbers of processes in the chemical industry involve heterogeneous catalysis, the use of homogeneous catalysis is more limited but expanding. Notable examples of homogeneous catalytic processes are the Wacker process,[1] which involves the palladium catalysed oxidation of ethene, and the Monsanto process which produces acetic acid from methanol *via* carbonylation involving a rhodium catalyst.[2] Such applications have attributed partly to the exponential growth in the synthesis and characterisation of metal-olefin, metal allyl, and metal alkyne complexes, which are important in catalytic processes,[3] and several reviews of the chemistry of these complexes have been published.[4-14]

The large number of studies has allowed standard organometallic reactions, such as ligand cleavage to generate 16-electron coordinatively unsaturated compounds, insertion, oxidative addition and reductive elimination, to be well documented. This in turn has allowed individual stage reaction schemes to be formulated for many catalytic processes, and the general chemical principles to be well understood.

Extension of the above studies has been directed to isoelectronic pseudo-allenes,[15-18] pseudo-alkynes, alkenes[19-22], and pseudo-allyls,[23] which contain hetero-atoms. It is the pseudo-allyls which we will be concerned with here, examples being given in Table 1.1.

Interest in catalytic processes involving small molecules involving hetero-atoms such as nitrogen,[40-41] has been directed to attempts to find routes to expensive organonitrogen chemicals, *e.g.* the commercial pathway to glutamic acid from

TABLE 1.1 Examples of pseudo-allyl ligands

Group	Name	References
>C - - - C - - - C<	allyl	
-N - - - N - - - N-	triazeno	24-27
O - - - C - - - O	carboxylato	28-31
S - - - C - - - S	dithiocarboxylate	32-33
>C - - - N - - - N-	hydrazones	34-35
-N - - - S - - - N-	sulphurdiimines	36
>C - - N - - - C<	aza-allyls	37-39
-N - - - C - - N-	amidino	

acrylonitrile.[42-43] Though much of the chemistry associated with the hydrocarbon ligands is also applicable to the iso-electronic hetero-atom group, account must also be taken of the chemistry of the hetero-atom. Thus whereas the allyl group often bonds to metals using its π-system, pseudo-allyls have the possibility of σ-bonding through the hetero-atom lone pairs, thus other coordination possibiliities exist.

Despite the catalytic interest and variety of bonding possibilities, the data on organonitrogen complexes is limited compared to that of the carbogroups, hence the need to study important pseudo-allyls such as amidines, which are discussed here in detail.

Amidines (Fig. 1.1) were first synthesised by Gerhardt[44] in 1858 by the reaction of aniline with CN-phenyl benzimidyl

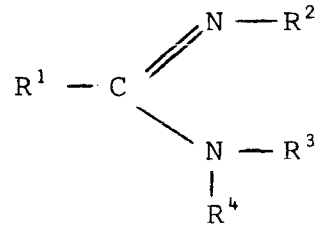


Figure 1.1

chloride. Amidines are named after the acid or amide which may be obtained from it after hydrolysis. Thus, when R^1 = H, the compound is known as formamidine; R^1 = CH_3, acetamidine; R^1 = C_4H_9, butylamidine; and R^1 = C_6H_5, benzamidine. It should be noted that the chemical literature systematically names amidines as amides of the corresponding imidic acid, *e.g.* hexanimidamide is the name of the amidine derived from hexanoic acid by replacement of the carboxyl group by $-C(:NH)NH_2$. Thus, acetamidine is ethanimidamide and formamidine is methanimidamide in the systematic literature.

1.2 Transition Metal Amidine Bonding Modes

The four types of metal to allyl group bonding modes (Fig. 1.2), are described below:

(a) σ-allyl: σ-bonded terminal carbon atom to the metal atom, localised double bond between the remaining carbon atoms, *e.g.* $(\sigma\text{-}CH_2{=}CHCH_2)Mn(CO)_5$,[45] $(\sigma\text{-}CH_2{=}CHCH_2)CpMo(CO)_3$.[46]

(b) μ-allyl: bridging between two metal atoms. The allyl group is σ-bonded to the first metal atom through a terminal carbon atom, and to the second metal atom by interaction of

the double bond, *e.g.* $(\mu\text{-}C_3H_5)_4Mo_2$,[47] and $[(\mu.C_3H_5)PtCl)]_4$.[48]

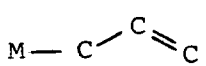
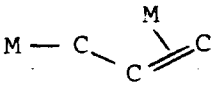
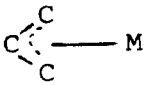
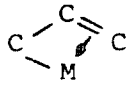
(c) <u>η^3-allyl</u>: delocalised bonding between three carbon atoms forming a multicentre bond with the metal. The three carbon atoms of the allyl group are in a plane above the metal, all metal to carbon distances are approximately equal, and the metal formally receives three electrons from the ligand, *e.g.* $(\eta^3\text{-}C_3H_5)Fe(CO)_3Cl$[49] $(\eta^3\text{-}C_3H_5)Mn(CO)_4$.[50]

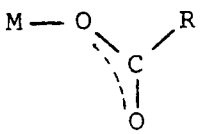
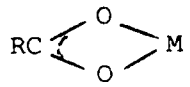
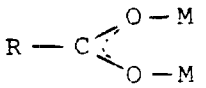
(d) <u>σ, η^3-allyl</u>: the group is bonded to the metal using a combination of σ and π bonds, *e.g.* $(\eta^3\text{-}C_4H_7)PdCl(PPh_3)$.[51]

Replacement of the two terminal carbon atoms of the allyl group with oxygen atoms gives the carboxylato group, and replacement of all three carbon atoms with nitrogens the triazeno group. The bonding modes are correspondingly modified (Fig. 1.2). The carboxylato-group can coordinate as (a) a monodentate ligand, *e.g.* $Co(O_2CCH_3)_2 4H_2O$;[28] (b) as a chelating ligand, *e.g.* $(\eta^6\text{-}C_6H_6)Mo(C_5H_5)(O_2CR)$[52]; (c) as a bridging ligand, (1) μ_2 bridging-(i) syn-syn, *e.g.* $[Pd_3(O_2CCH_3)_6(0.5H_2O)$;[30] (ii) syn-anti *e.g.* $Cu(O_2CH_2)$,[53] (iii) anti-anti, *e.g.* $Mn(O_2CMe)_2(H_2O)_4$;[54] (2) monatomic bridging, *e.g.* $Hg(O_2CMe)[(C_6H_{11})_3P]$;[55] (3) additional bridging, *e.g.* $Cu(O_2CMe)$;[56] and (4) mixed arrangements involving chelation and bridging, *e.g.* (a) MeTl(O_2CMe),[53] or (b) $Cd(O_2CMe)_2(H_2O)_2$.[58] These bonding modes are discussed in detail in several reviews.[59-61]

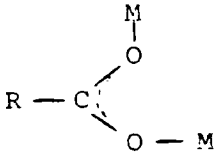
The triazino-group shows (a) monodentate, *e.g.* $Pt(PPh_3)_2(PhN_3Ph)_2$,[62] (b) chelating, *e.g.* $CpMo(CO)_2(ArN_3Ar)$[63] and (c) bridging, *e.g.* $Ni_2(\mu\text{-}ArN_3Ar)_4$[64] modes of bonding (Fig.1.2). All have been established by X-ray crystallography.

Figure 1.2 Allyl and Pseudo-Allyl Bonding Modes

(1) ALLYL (a)  (b)  (c)  (d) 

(2) CARBOXYLATO (a)  (b)  (c) (1) 

(i)



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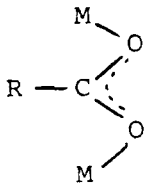
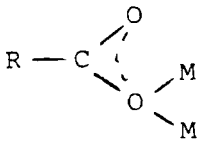
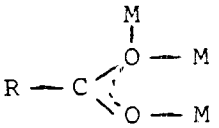
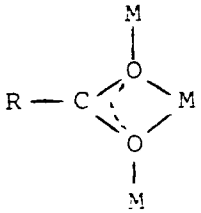


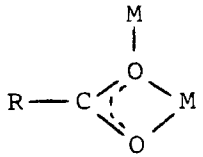
(iii)

(2) 

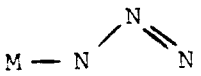
(3) 

(4) 

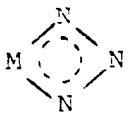
(a)



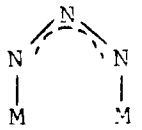
(b)

(3) TRIAZENO 

(a)



(b)



(c)

For the amidines many of the possible bonding modes illustrated in Figure 1.3 have been established by X-ray methods. We shall discuss amidino-complexes, the synthetic methods used to produce them; structural aspects; and industrial applications in the course of this review. The bonding modes are:

(a) Monodentate: one nitrogen is σ-bonded to the metal, the other is not attached but has a localised double bond to the central carbon atom. Two compounds have been characterised by X-ray crystallography - $PtC_6H_3(CH_2NMe_2)_2(C_{15}N_2H_{15})$,[65] and HgC_6H_5[p-tolylNC(H)N p-tolyl].[66]

(b),(c),(d) Chelate Complexes: the relatively small size of the four-membered ring, introduces steric strain and distortion of the valency angles. The class may be subdivided as follows (i) σ, σ-symmetrical attachment; bonding delocalised *e.g.* $Pt[PhNC(Ph)NPh]_2$,[67] which has been characterised by X-ray crystallography, (ii) σ, σ-unsymmetrical attachment, one nitrogen σ-bonds to the metal, whilst the other donates to the metal *via* its lone pair of electrons, *e.g.* $MeTaCl_2\{C_6H_{11}NC(Me)NC_6H_{11}\}_2$, which has been characterised by X-ray crystallography,[68] (iii) one nitrogen σ-bonds to the metal whilst the localised double bond interacts in an alkene type manner. No amidine complexes of this type have been characterised.

(e) η^3-Allyl: this type of amidine linkage is not yet known.

(f),(g) Bridging: this involves incorporation of another metal in the ring. The metal atoms may be the same as in $Mo_2\{PhNC(Ph)NPh\}_4$,[69] or different as in [[2,6$(Me_2NCH_2)_2C_6H_3$] [p-tol NC(H)N i-Pr] Pt Hg Br Cl].[70]

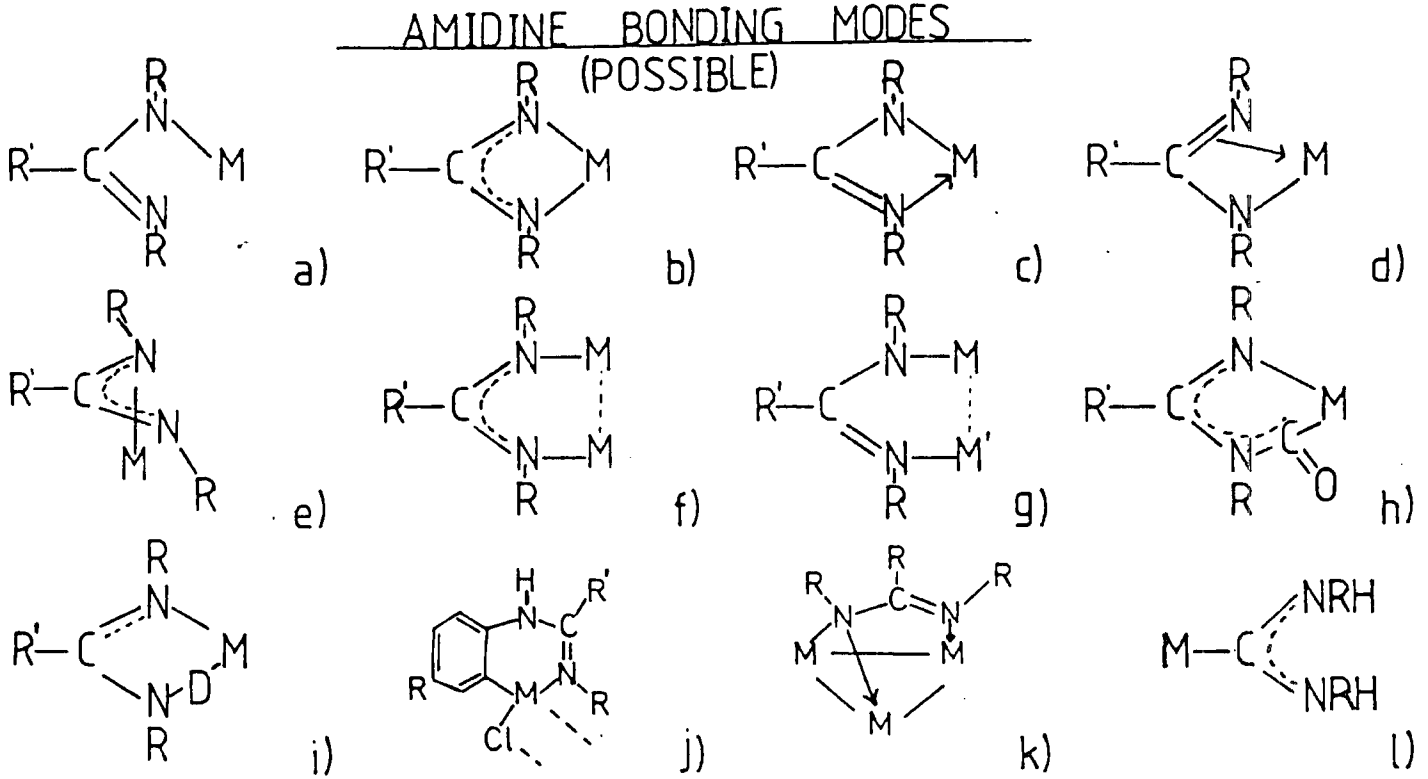


FIGURE 1.3

(h),(i) Carbamoyl/Insertion Complexes: insertion of a carbonyl group into the metal to nitrogen amidine bond results in a complex known as a carbamoyl, *e.g.* $Re(CO)_4$ CONPhC(Ph)NPh .[71] Insertion of CH_2, and C_6H_5CN has also been found. In the first case CH_2 is inserted between the metal to nitrogen bond of a chelating amidine, in the complex $[W_2(\mu\text{-}CO)_2\{\mu\text{-}HC(N\text{-}3,5\text{-}xylyl)_2\}_2\{HC(N\text{-}3,5\text{-}xylyl)_2\}\{(N\text{-}3,5\text{-}xylyl)CH(N\text{-}3,5\text{-}xylyl)\text{-}CH_2\}]$.[72] In the latter case the treatment of $Pt(PhCN)_2Cl_2$ with $HN(Li)C(C_6H_5)NH$ results in nucleophilic attack at the nitrile to form $Pt\{HNC(C_6H_5)NC(C_6H_5)NH\}_2$ which involves a six-membered ring. The structure has been established by crystallography.[73]

(j) *O*-Metallation: if a nitrogen substituent is aryl, *ortho* metallation may occur forming a reasonably stable six-membered ring. Also if the central carbon substituent is aryl o-metallation can occur here to give a five-membered ring. A six-membered ring has been established for $(\pi\text{-}Cp)Pd\{p\text{-}tolyl\text{-}N(H)C(CH_3)N\text{-}p\text{-}tolyl\}$,[74] and a five-membered ring has been indicated in $Re(CO)_3\{PhNC(C_6H_4)NHPh\}\{PhNC(Ph)NH\}$ by spectroscopic methods.[74]

(k) Cluster-Capping: The X-ray structure of $[Os_3(\mu\text{-}H)(CO)_9\{NPhC(Ph)NH\}]$,[75] shows the amidino-ligand capping one triangular face of osmium atoms, and formally donating five electrons to the cluster.

(l) Carbene: this mode of bonding was simply included for the sake of completeness, since the complexes should be regarded more as carbenes than as amidino-complexes. One example is $(CH_3NC)_4Ru\text{-}C(NHCH_3)_2^{2+}$.[76]

The amidine ligand may also form simple salts, *e.g.* $[PhC(NH_2)_2]$ $[cis\text{-}(OC)_4Re(CH_3CO)_2]$,[77] which has been established by crystallography.

1.3 Synthetic Methods for Amidine-Transition Metal Complex Production

For the synthesis and properties of the ligands there are three extensive reviews.[78-80] The general methods employed for the synthesis of amidine-transition metal complexes are as follows:

(a) Reaction of a lithiated amidine with a transition-metal halide *in situ*,[61] *e.g.*

n-butyl Li + [PhN(H)C(R)NPh] $\xrightarrow{\text{ether}}$ [PhN(Li)C(R)NPh]

yellow, air, and moisture sensitive.

$2PhN(Li)C(R)NPh + Pt(PhCN)_2Cl_2 \longrightarrow Pt(PhNC(R)NPh)_2$ + 2 LiCl or another group la salt, *e.g.*[81]

$K(HC(NAr)_2) + CpMo(CO)_3Cl \longrightarrow CpMo(HC(NAr)_2)(CO)_2$ + KCl + CO.

(b) By the reaction of an amidine with a metal halide[82], *e.g.*

$(Cp)Mo(CO)_3Cl + 2PhNHC(CH_3)NPh \longrightarrow CpMo(CO)_2\text{-}\{CH_3C(NPh)_2\} + [CH_3C(NHPh)_2]^+Cl^-$.

(c) By the reaction of an amidine with metal carbonyls in air causing displacement of the carbonyl groups, *e.g.*[69]

$2Mo(CO)_6 + 4PhHNC(Ph)NPh \xrightarrow{\text{air}} Mo_2[PhNCNPh]_4 + 12CO + 4H_2O$.

(d) By the displacement of silver halides from the reaction of silver amidines with metal halides, *e.g.*[83]

$$Ag\{HC(NPh)_2\} + CpMo(CO)_3Cl \longrightarrow CpMo(CO)_2\{HC(NPh)_2\} + AgCl + CO.$$

(e) The reaction of carbodiimide with a metal hydride, *e.g.*

$$OsH_2(CO)(PPh_3)_3 + Pr^iN = C = NPr^i \longrightarrow OsH\{Me_2CHNC(H)NCHMe_2\}(CO)(PPh_3)_2 \xrightarrow[\text{dehydrogenation}]{\text{heat}} OsH[CH_2=C(Me)NC(H)NCHMe_2]-(CO)(PPh_3)_2.$$ [84]

(f) The use of copper amidines,[81] *e.g.*

$$MoCp(CO)_3Cl + Cu[HC(N\text{-}p\text{-}tolyl)_2] \xrightarrow[R.T./1\ week]{C_6H_6} \{MoCp[HC(N\text{-}p\text{-}tolyl)_2](CO)_2\} + CuCl + CO.$$

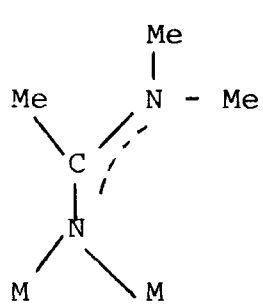
1.4 Amidine-Complexes

(A) Ti, Zr: Dialkyl amides react with acetonitrile to give dark brown, air-sensitive, insoluble compounds,[85]

$$M(NMe_2)_x + yCH_3CN \longrightarrow M\{N{:}C(Me)NMe_2\}_2(NMe_2)_{x-y}$$

M = Ti, Zr, Ta. Characteristic N ═ C ═ N i.r. band 1577-87 cm^{-1}.

The postulated structure is: (Fig.1.4)



(Figure 1.4)

(B) Nb and Ta: (see above). The reaction of $ClMe_xMCl_{5-x}$ (M=Nb, Ta; n=1,2,3), with carbodiimides RNCNR, (R=isopropyl, cyclohexyl, p-tolyl), gives products of the types: $MCl_4\{RN\text{-}C(Me)=NR\}$, $MeMCl_3\{RNC(Me)=NR\}$, $MCl_3\{RNC(Me)=NR\}_2$.

Infra-red $\nu(C\overset{---}{=}N)$ bands were observed at 1635-1506 cm^{-1}.[86] A number were later characterised by X-ray crystallography.[169-172]

Other Tantulum and Niobium complexes have been synthesised by reacting acetamidine hydrochloride with the M(V) chlorides (M=Ta or Nb) in the presence of a large excess of acetonitrile. The resultant $[CH_3C(NH_2)_2]MCl_6.2CH_3CN]$ compounds react further with KSCN yielding $[CH_3C(NH_2)_2]M(NCS)_6.2CH_3CN$.[87]

(C) Cr,Mo, and W: a number of carbonyl displacement reactions have been carried out, but with mixed success.

$$2M(CO)_6 + 8\{RN(H)C(R)NR\} \longrightarrow M_2[RNC(R)NR]_4 + 12CO + 4H_2.$$

(M=Cr,Mo and W; amidine = N,N´ disubstituted formamidines, acetamidines and benzamidines). The formamidine complexes were investigated by Vrieze.[88] The tungsten derivative was not W_2 (amidinato)$_4$ as expected but $[W_2(\mu\text{-}CO)_2\{\delta\text{-}HC(NR)_2\}_2\{(N\text{-}R)CH(N\text{-}R)CH_2\}]$, a novel complex containing a CH_2 group in a chelating formamidino group, two bridging carbonyl groups, and two bridging formamidino groups. The structure was confirmed by X-ray crystallography.[72] The reaction of the above tetrakisamidine complexes with more hexacarbonyl yielded (1) Mo; $Mo_2\{HC(NR)_2\}_2\{HC(NR)\cdot Mo(CO)_3\}_2$ and $Mo_2\{HC(NR)_2\}_3\{HC(NR)\cdot Mo(CO)_3\}$, and (2) Cr; only $Cr_2\{HC(NR)_2\}_3\{HC(NR)\cdot Cr(CO)_3\}$. The $M(CO)_3$ fragment is bonded to one of the aromatic groups. Monomer-dimer equilibria are shown by the complexes in solution, and are very dependent on R.

With benzamidines, the tetrakisdimolybdenum compound has been determined crystallographically.[69] The chromium product was a red insoluble crystalline material which analysed as Cr_2 (amidinato)$_4$.[69] The tungsten reaction gave a red crystalline solid which was not fully characterised.[69]

The tetraethylammonium salts of the formamidino-metal carbonyl anion $[M(CO)_4\{HC(NR)_2\}]^-$ (M=Cr, Mo or W, R=aryl, t-but), have been made *via* the 1:1 reaction of $NEt_4[M(CO)_5Cl]$ with potassium formamidines.[89] The reaction of $NEt_4[M(CO)_5Cl]$ with N,N´dimethylforma midine yielded the carbamoyl derivative $NEt_4[M(CO)_4\{MeNCHN(CO)Me\}]$ (M=Cr, Mo, W). Fluxional behaviour of the terminal carbonyls is indicated by ^{13}C n.m.r., and when heated with triphenylphosphine or pyridine, carbonyl substitution occurs to give fac $NEt_4[M(CO)_3L\{HC(NR)_2\}]$ (M=Mo, W) (L = PPh_3, Py).

Cotton found amidines to be ideal for the promotion of metal-metal bonding because of their bridging characteristics. The complexes were produced by the reaction of lithioamidines with tetrakis acetate-metal complexes. The complexes were identified by X-ray crystallography and accurate mass, mass spectrometry. The following were prepared: (i) $Cr_2(CH_3N(Ph)-NCH_3)_4$;[90] (ii) $Mo_2\{[(2,6\text{-xylyl})N]_2(CCH_3)_2\}(CH_3CO_2)_2$ 4THF;[91] (iii) $Mo_2\{(PhN)_2CCH_3\}_3(CH_3CO_2)$;[91] (iv) $W_2\{(PhN)_2CCH_3\}_2$ $(dmph)_2$ 2THE;[92] (dmph = the anion of 2,4-dimethyl-6-hydroxy-pyrimidine).

Cyclopentadienyl metal amidine complexes have been well studied, Vrieze documenting the formamidines, Kilner the formamidines, acetamidines and benzamidines, and Brunner the optically active benzamidines.

Molybdenum and tungsten formamidine cyclopentadienyl complexes were produced by a number of routes, the molybdenum reactions being the most extensively studied:

(1) $MoCp(CO)_3Cl + K\{HC(N\text{-p-tolyl})_2\} \xrightarrow[RT/1hr.]{C_6H_6} MoCp\{HC(N\text{-p-tolyl})_2\}(CO)_2 + MoCp\{HC(N\text{-p-tolyl})N(CO)\text{-p-tolyl}\}(CO)_2 + KCl + CO.$

The product complexes were separated by chromatography, the latter being of the carbamoyl type.

(2) $MoCp(CO)_3Cl + M'\{HC(N\text{-}p\text{-}tolyl)_2\} \xrightarrow[\text{RT/1 week}]{C_6H_6} MoCp\{HC(N\text{-}p\text{-}tolyl)_2\}(CO)_2 + M'Cl + CO.$

$\{MoCp(CO)_3\}_2 + 2M'\{HC(N\text{-}p\text{-}tolyl)_2\} \xrightarrow[\text{reflux 1-2 weeks}]{\text{benzene}} 2\ MoCp\{HC(N\text{-}p\text{-}tolyl)_2\}(CO)_2 + 2M' + 2\ CO.$

(3) $MoCp(CO)_3Cl + 2\ HC(N\text{-}p\text{-}tolyl)(NH\text{-}p\text{-}tolyl) \xrightarrow[\text{RT/24 hrs.}]{h\nu/\text{benzene}} MoCp\{HC(N\text{-}p\text{-}tolyl)\}_2(CO)_2 + \{HC(NH\text{-}p\text{-}tolyl)_2\}Cl\downarrow + CO.$

M' = Cu or Ag.

(4) $MCp(CO)_3Cl$ + N,N'dimethylformamidine ⟶ $[MCp\text{-}\{HC(NMe)N(CO)Me\}(CO)_2 \xrightarrow{h\nu} [MCp\{HC(NMe)_2\}(CO)_2]$.

(M = W or Mo).[109]

Using symmetrically substituted potassium formamidines $MCp\{HC(NR)_2\}(CO)_2$ and $MCp\{HC(NR)N(CO)R\}(CO)_2$ were formed.[93] Separation was carried out by column chromatography, (M=Cr, Mo and W). The novel chromium analogues were prepared "*in situ*" from $CrCp(CO)_3I$. One complex $WCp\{HC(NPh)N(CO)Ph\}(CO)_2$, showed terminal CO exchange on the N.M.R. time scale; the others were stereochemically rigid. Product relative molar ratios were found to be highly dependent on the molar ratios of the starting materials. As an extension to this work, complexes of the type $[MCp\{HC(N\text{-}p\text{-}tolyl)_2\}(CO)L]$, (M=Mo, W; L=$PPh_3$, $AsPh_3$, $SbPh_3$, $P(OPh)_3$, $P(OMe)_3$) were prepared by the reaction of $MCp(CO)L_2Cl$ with potassium N, N' di-p-tolylformamidine.[94] The reaction of the dimer $\{MCp(NO)X_2\}_2$ (X=Cl, Br, I) with the parent formamidine yielded the complexes $MoCp\{HC(N\text{-}p\text{-}tolyl)_2(NO)X\}$. The effects of both L and X on ^{13}C N.M.R. frequencies were noted, L appearing to cause a lack of correlation

in ^{13}C-CO frequencies which had previously been found for $M(CO)_5L$ complexes.

Kilner,[82,95-97] found that both lithioamidines and parent amidines, reacted with various metal cyclopentadienyl complexes (M=W and Mo) in the following ways:

(i) $MoCp(CO)_3Cl + Li\{RNC(R)NR'\} \longrightarrow \{MoCp(CO)_2 - CON(R')C(R)NR'\}$ or $H_2NC(Ph)NH$ (I)

yellow/carbamoyl

(R=H, R' = Ph; R = Me, R' = H, Ph, p.tolyl; R=Ph,R'=Me).

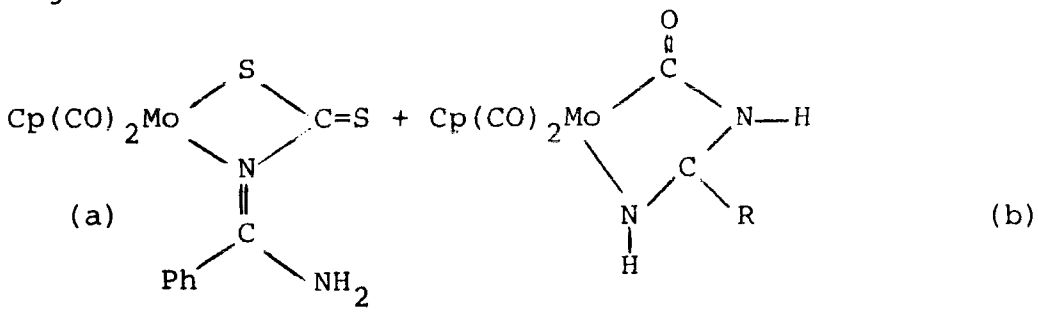
(ii) $MoCp(CO)_3Cl$ + N,N'disubstituted amidine $\longrightarrow$ $MoCp(CO)_2(R'NC(R)NR')$ (II)

(iii) $MoCp(CO)_2(PPh_3)Cl + Li\{R'NC(R)NR'\} \longrightarrow$ (II)

It is postulated that the mechanism in (i) is that of nucleophilic attack at a carbonyl group, and that of attack at the metal centre in (ii). Decarbonylation from (I) to (II) was achieved in small yields by thermolysis and photolysis. I.R. data supported the generation of $[CpMo(CO)_3\{RNCRN(Me)R'\}]^+I^-$ in photolytic reactions carried out in the presence of methyl iodide. Attempts to insert carbon monoxide into $MCp(CO)_2$ - (amidinato) bonds (M=W and Mo), proved unsuccessful.[97] The N,N'diphenylbenzamidino complex was characterised by X-ray crystallography.[98]

Brunner though his interest in asymmetric catalysis has studied a number of optically active molybdenum cyclopentadienyl amidinato-complexes.[99-108] The reaction of $MoCp(CO)_3Cl$ with an N,N'disubstituted amidine in pyridine gave $MoCp(CO)_2$ (amidinato) complexes. Work with lithioamidines described products similar to those previously formed by Kilner.[98] Brunner also found that the reaction of lithiated amidines, carbon disulphide

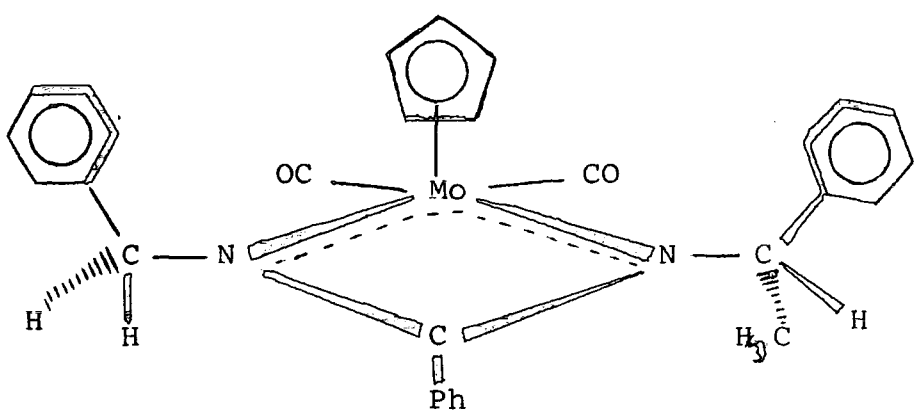
and $MoCp(CO_3)Cl$ results in the formation of (a) and (b) in Figure 1.5.



(Figure 1.5)

(R = Me and Ph; when R=Ph only (a) was formed).

$MoCp(CO)_3Cl$ and amidines reacted to form type (II) complexes. By using optically active amidines the Mo becomes an asymmetric centre, and pairs of diastereoisomers are formed. With racemic chiral amidines diastereoisomeric pairs of enantiomers were obtained and separated by fractional crystallisation. The conformations of the complexes were determined by various methods, *viz.* X-ray crystallography, ^1H high-field nuclear Overhauser effect difference spectroscopy, and circular dichroism measurements. Of the four optically active compounds determined by X-ray crystallography, the configuration (a) (Fig. 1.6) was the most preferred:



(a)

(Figure 1.6)

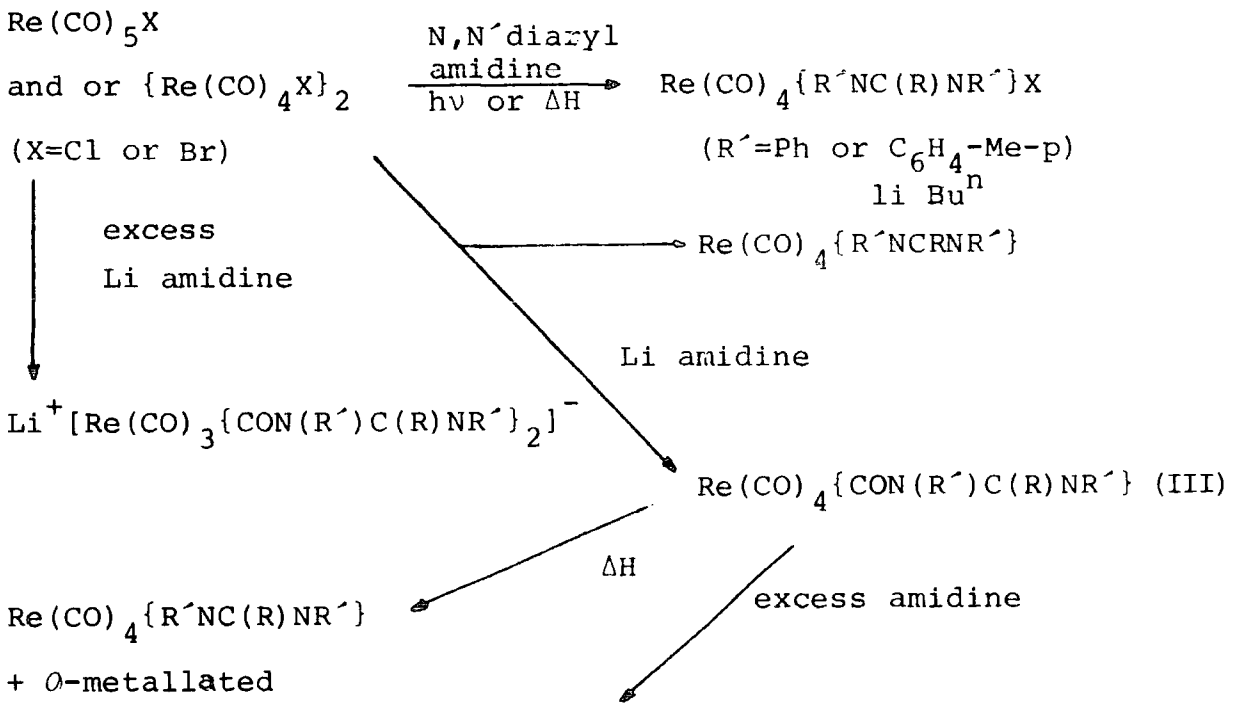
The importance of this work lies in the field of asymmetric catalysis in particular in providing insight into the way in which chiral information may be transmitted.

(D) Mn and Re: Kilner[97,109,110] found that the reaction of lithioamidines with $Mn(CO)_5X$ (X=Cl, Br, or I) yielded the carbamoyl complexes $Mn(CO)_4$ {CO.N(R´).C(R).NR´}. The failure to insert CO into Mn-N amidine bonds, favours a mechanism proceeding by nucleophilic attack at a carbonyl group of $Mn(CO)_5Br$. In contrast to other carbamoyls, these amidinocarbamoyl groups can be decarbonylated by U.V. irradiation to form $Mn(CO)_4$ {R´NC(R): NR´} complexes. Thermolysis of the carbamoyls also caused decarbonylation, but when achieved under a high pressure of carbon monoxide the first example of an amino-manganese carbonyl complex $Mn(CO)_5$ {N(Ph).C(Ph):NPh} was also formed.

Abel,[111] has investigated the analogous formamidine complexes. Both the monomeric and the dimeric carbonyl halides $Mn(CO)_5X$ and $\{Mn(CO)_4X\}_2$ yield $Mn(CO)_4$\{RNCHNR\} complexes. Using analogous rhenium monomeric and dimeric carbonyl chlorides, similar carbamoyl and formamidino complexes to those described above for manganese were formed.

Cotton,[112] as part of his studies in metal-metal bonding, reacted tetrabutylammonium octachlorodirhenate and the amidines N,N´diphenylacetamidine and N,N´dimethylbenzamidine in the melt to yield $Re_2Cl_4\{(PhN)_2CCH_3\}_2$ and $Re_2.\{(MeN)_2CPh\}_4Cl_2CCl_4$ respectively. The complexes were characterised by mass spectroscopy and X-ray crystallography.

Kilner[71,74] has extensively investigated rhenium carbonyl complexes of the N,N´diarylamidines, *viz.*



(R´´=H or Me.

$Re_2(CO)_{10}$ + N,N´diarylamidine $\xrightarrow{\text{reflux}}$ $Re(CO)_4\{R´NC(R)NR´\}$.

$Re(CO)_3$ (L){R´NC(R)NR´} (IV) complexes were prepared by decarbonylation of (III) or by the reaction of $Re(CO)_4LBr$ with amidines in refluxing toluene (L=PPh_3 or $AsPh_3$). The reaction stops at the intermediate compound $Re(CO)_3(PPh_3)\{R´NC(R)$-$N(Me)R´\}Br$ when an NNN' trisubstituted amidine is used. Related complexes to this were made by reacting (IV) with hydrobromic acid.

$Re(CO)_5X$ + amidine $\xrightarrow[\text{reflux}]{\text{monoglyme}}$ $Re(CO)_3\{R´NC(R)NHC_6H_3R´´$-p$\}$ {R´NC(R)NHR´} (R=H,R´=Ph; R´´=H; R=Me or Ph, R´=C_6H_4Me-p, R´´=Me; R=Me or PhR´=Ph, R´´=H). These complexes contain six-membered *O*-metallated rings. Benzamidines (R=Ph) produce in addition isomeric complexes in which *O*-metallation of the skeletal carbon substituent occurs to give complexes having five-membered *O*-metallated rings. A 1,3-proton shift mechanism for *O*-metallation was eliminated, and the complexes and their reaction schemes were discussed on the basis of I.R.

and ^{1}H and ^{13}C N.M.R. data. Elemental analysis and mass spectroscopy were also used to characterise the complexes.

Toniolo[173] found that $Re(CO)_3(PPh_3)_2$ reacts with Li{ArNC(H)NAr}, (Ar=p-$CH_3C_6H_4$, C_6H_5, p-Cl C_6H_4, o-F·C_6H_4) in boiling T.H.F. to yield the complexes $Re(CO)_2(PPh_3)_2$ - {ArNC(H)NAr}. Significant I.R. bands in the 1620-1218 cm^{-1} region indicated an N-C-N delocalised system. One of the complexes (Ar=Ph) was shown by X-ray crystallography to have a symmetrically bound delocalised amidino group.

Recently the benzamidinium salt of a rheniumacetylacetonate anion was characterised by X-ray crystallography.[77]

(E) Fe, Ru, and Os: the studies of iron amidines have been limited by the very unstable and difficult to characterise complexes.

(1) $CpFe(CO)_2Cl$ + Li amidine ⟶ unstable product - difficult to characterise[114]

(2) $Fe(CO)_4X_2$ + Li amidine ⟶ "$Fe(CO)_4[(NR)_2C(R)]$" ↓ Al_2O_3 $Fe(CO)_4${RN(H)C(R)NR}

(X = Br or I)

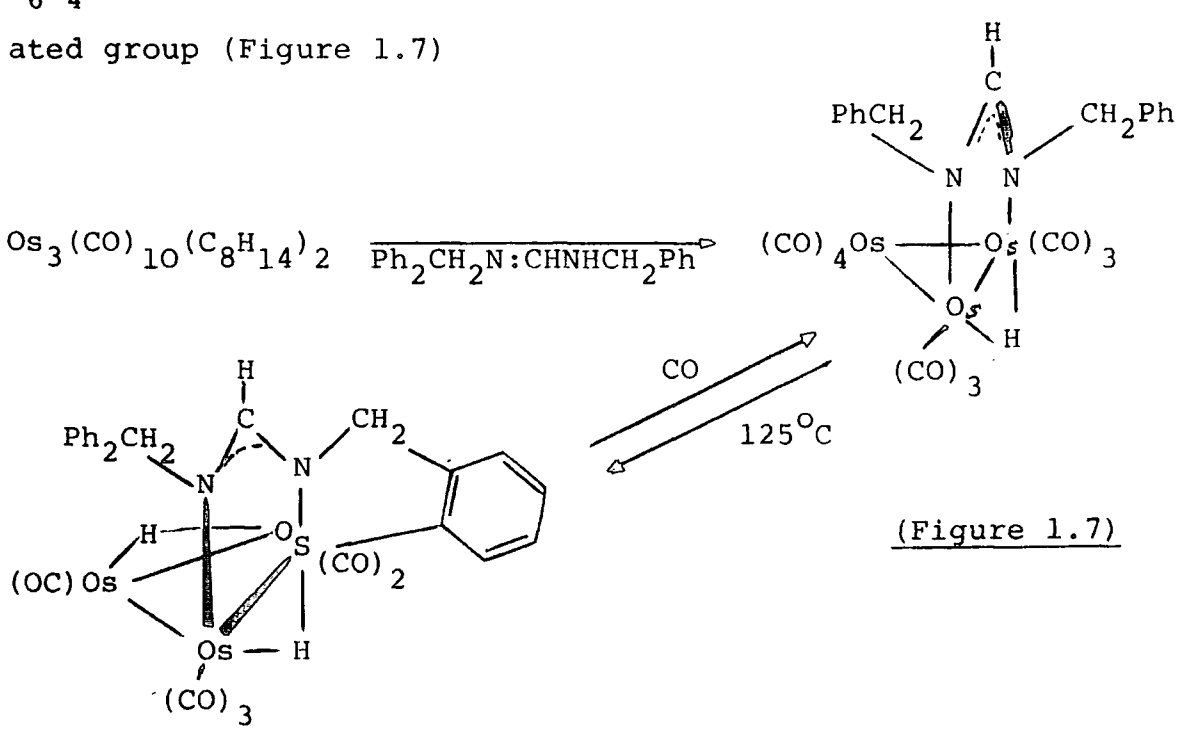
The above formulations are based mainly on infra-red data, the complexes being air, moisture and thermally sensitive.[113]

Iron (III) chloride and iron (II) chloride react with R´N(Li)C(R)NR´ (R=CH_3, R´=Ph) to produce high spin $Fe\{R´NC(R)NR´\}_3$ and polymeric $[Fe\{R´NC(R)NR´\}_2]_3$ respectively. The complexes failed to react with, or were decomposed by, a number of reducing electrophilic and nucleophilic reagents. The exception was the blue $Fe\{p\text{-}CH_3C_6H_4NC(CH_3)(N\text{-}p\text{-}CH_3C_6H_4\}_3$ complex which reacted readily with nitric oxide to form a purple addition complex from which the N-nitroso-compound

$[p\text{-}CH_3C_6H_4NC(CH_3)N(NO)\text{-}p\text{-}CH_3C_6H_4]$ was obtained.[114]

Hieber,[115] obtained amidine salts from the reaction of the dimers $[M(NO)_2Br]_2$ with N-phenylbenzamidine, (M=Fe,Co) formulated as $\{(ON)_2M(H_2NC(Ph)NPh\}^+Br^-$.

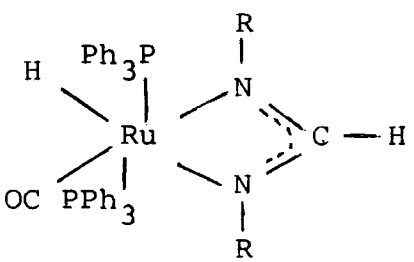
Robinson,[184] found that the reactions of carbodiimides ($Pr^iN{=}C{=}NPr^i$) with $[RuH(X)(CO)(PPh_3)_3]$ (X=Cl, Br) complexes in refluxing benzene involved insertion of the carbodiimide into the Ru-H bond and concomitant dehydrogenation of an isopropyl group to yield the complexes $[RuX\{CH_2\text{-}C(Me)\text{=}N \overset{--}{=} CH \overset{--}{=} NCHMe_2\}(CO)(PPh_3)_2]$. The chelate nature of the ligand was established by X-ray crystallography. He found also that $OsH_2(CO)(PPh_3)_3$ reacted with $Pr^iN = C = N\text{-}Pr^i$, [84] to afford the intermediate $OsH(Me_2HCN \overset{---}{=} CH \overset{--}{=} NCHMe_2)(CO)(PPh_3)_2$ which, on further heating, dehydrogenates to yield $[OsH\{CH_2 = C(Me)N \overset{--}{=} CH \overset{--}{=} NCHMe_2\}(CO)(PPh_3)_2]$. Some osmium clusters have amidines as capping ligands. N,N dibenzyl- or diisopropyl-formamidines react with $Os_3(CO)_{12}$ and $Os_3(CO)_{10}(cyclooctene)_2$ to yield $HOs_3(CO)_9(i\text{-}PrNCHN i\text{-}Pr)$ and $H_2Os_3(CO)_9(PhCH_2NCHNCH_2\text{-}C_6H_4)$ respectively,[116] the latter containing an *ortho*-metallated group (Figure 1.7)



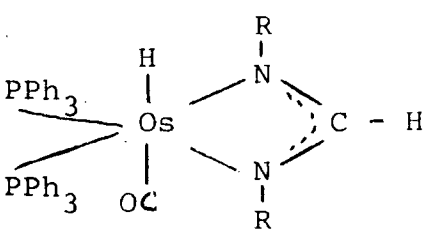
(Figure 1.7)

Lewis[75] reacted $Os_3(CO)_{10}(NCMe)_2$ with amidines yielding the complexes $Os_3(\mu\text{-}H)(CO)_{10}\{NCH(Me)NH\}$ and $Os_3(\mu\text{-}H)(CO)_{10}\{NPhC(Ph)NH\}$. The complexes were thermally decarbonylated to the monocarbonyls, one of which $Os_3(\mu\text{-}H)(CO)_9(MeCN_2H_2)$ exists in tautomeric form. $Os_3(\mu\text{-}H)(CO)_9\{NPhC(Ph)NH\}$ was characterised by X-ray crystallography.

Treatment of $[MH_2(PPh_3)_4]$ M=Ru or Os, with p-tolyl isocyanate yielded the formamidinato compounds $MH\{RNC(H)NR\}(CO)(PPh_3)_2$.[117-8] The ruthenium complex was found to be the same as that synthesised previously using di-p-tolyl carbodiimide.[84] However, the less labile osmium complex, rather than isomerising to the thermodynamically more favoured structure (V), which is preferred by the ruthenium complex, prefers structure VI, (Fig. 1.8).



(V)



(VI)

(Figure 1.8)

The formation of the formamidinato ligand is thought to involve the fragmentation of at least two isocyanates; and the overall stoichiometry:

$$RuH_2(PPh_3)_4 + 2RNCO \longrightarrow RuH\{RNC(H)NR\}(CO)(PPh_3)_2 + PPh_3 + OPPh_3$$

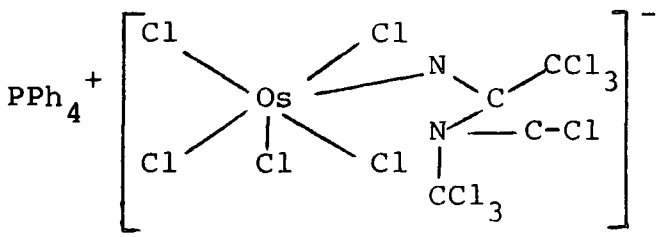
or

$$OsH_4(PPh_3)_3 + 2RNCO \longrightarrow OsH\{RNC(H)NR\}(CO)(PPh_3)_2 + OPPh_3 + H_2$$

Robinson[174] has also investigated the reaction of the

carbodiimide ($Pr^iN=C=N-Pr^i$) with several types of hydrides to afford products containing the bidentate N,N´di-p-tolyl-formamidinato ligand-L. The hydrides $[MHX(CO)(PPh_3)_3]$ (M=Ru, Os; X=Cl, Br, or $OCOCF_3$), $[MH_2(CO)(PPh_3)_3]$, $[RuH_2(PPh_3)_4]$, $[OsH_4(PPh_3)_3]$, $[IrHCl_2(PPh_3)_3]$, (trans chlorides), and *mer*-$[IrH_3(PPh_3)_3]$ yielded the complexes $(MX(L)(CO)(PPh_3)_2]$, (two isomers), $[MH(L)(CO)PPh_3)_2]$, $[M(L)_2(PPh_3)_2]$, $[Ir.Cl_2(L)(PPh_3)_2]$ and $[IrH_2(L)(PPh_3)_2]$ respectively. The structures and stereochemistry of the new complexes was determined by ^1H and ^{31}P N.M.R. The structure of trans $[RuH(L)CO(PPh_3)_2]$ was determined crystallographically.

Osmium pentachloride reacts with trichloroacetonitrile in the presence of chlorine yielding $Cl_4Os[NC(CCl_3)NCCl(CCl_3)]_2$, which undergoes an exchange reaction with PPh_4Cl to produce $PPh_4[Cl_5Os\{NC(CCl_3)NCCl(CCl_3)\}].CH_2Cl_2$. It has the following interesting structure (Fig. 1.9)



(Figure 1.9)

(F) Co, Rh, Ir: (See Ru), Olsen,[120] has determined the structure of acetamidinium tetrachlorocobaltate, in which each cation is shared by two anions thus forming an infinite two-dimensional array.

Minghetti[121] has compared the direct addition of two different N,N diarylformamidines L=(H-C=N(Ar)(NH(Ar), to metal salts. It was found that when Ar = p-nitrophenyl, the amidine was unreactive, reaction with cadmium bromide, zinc bromide, cobalt chloride, $[(CO)_2Rh\ Cl]_2$ or silver fluoro-

borate yielding no complex derivatives. However when Ar=p-tolyl, the following formed; L_2CoCl_2 (blue); $[LH_2][CoCl_4]$ (turquoise); $(CO)_2RhClL$ (pale yellow); L_2ZnBr_2 (white); L_2CdBr_2 (white); $L_3Cd_2Br_4$ (white); $LHgCl_2$ (yellow); $[L_2Ag]^+ BF_4^-$ (white); and L_2AgNO_3 (white). The inactivity of the p-nitrophenyl substituted formamidine was explained by the electron withdrawing group in the aromatic ring.

Attempts by Kilner[122] to use the lithio amidine route have proved unsuccessful,

$CoCl_2$ + Li amidine $\xrightarrow{\text{monoglyme}}$ light blue solid + Li Cl (inseparable)

$Rh(\eta^5\text{-}C_5Me_5)Cl(RNC(R')NR)$ (VII), where R'=H or Me was prepared from the reaction of $[Rh_2(\eta^5\text{-}C_5Me_5)Cl_4]$ with [RN(H)C(R')NR] in the presence of base, or by reaction with Ag(RNC(R')NR) or K(RNC(R')NR).[123-4] The reactions of (VII) have been extensively studied:

(VII) $\xrightarrow{CS_2}$ $[Rh(\eta^5\text{-}C_5Me_5)Cl[SC\{N(p\text{-tolyl})CHN(p\text{-tolyl})S\}]$. dithio carbamate

(VII) $\xrightarrow{CO}$ $[Rh(\eta^5\text{-}C_5Me_5)Cl[CO\text{-}N(p\text{-tolyl})CHN(p\text{-tolyl}]$. carbamoyl.

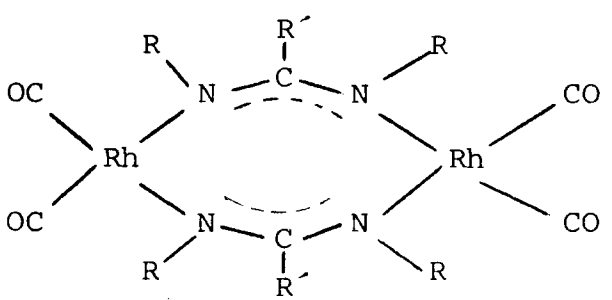
(VII) $\xrightarrow{Ag[PF_6] + L.}$ $[Rh(\eta^5\text{-}C_5Me_5)Cl\{PhN{=}{=}C[N\text{-}p\text{-tolyl}]CHN[p\text{-tolyl}]\}S$ thiourido. (structure characterised by crystallography).

(VII) $\xrightarrow{Ag[PF_6] + L.}$ $[Rh(\eta^5\text{-}C_5Me_5)L[RNC(CH_3)NR][PF_6]$. (L = MeCN or PPh_3, R=p-tolyl).

Piraino[125] synthesised [Rh(diol)(formamidine)]$_2$ (diol = cycloocta-1,5-diene, (VIII); diol = norbornadiene (IX);

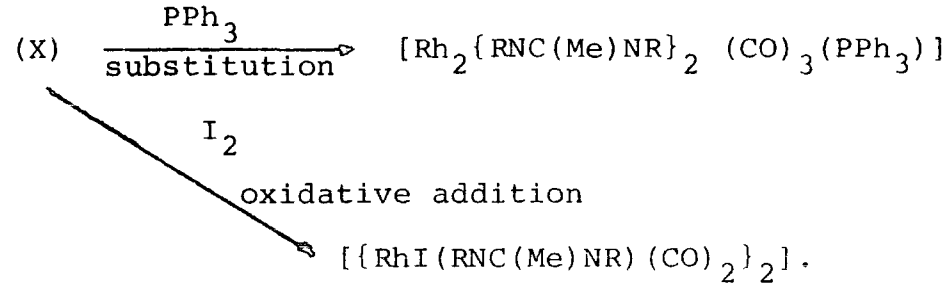
formamidine = N,N´di-p-tolylformamidine). The complexes are dimeric and bridged by the formamidine ligand. The complexes react with carbon monoxide, bis(1,2-diphenylphosphino)ethane (dppe) and PPh_3 with displacement of the diene ligand to yield $[Rh(CO)_2\{RNC(H)NR\}]_2$, $[Rh(dppe)_2]^+$ and $[Rh(PPh_3)_2\{RNC(H)NR\}]$ respectively. The latter complex was only isolated as an O_2 adduct. With HCl or HBF_4(aq.), (VIII) and (IX) form the formamidino cation [p-tolyl NHC(H)NH-p-tolyl]$^+$ and $[Rh(diol)X]_2$ X=Cl,F. $[Rh(C_8H_{12})$ formamidine$]_2$ reacts with CS_2, SO_2, PhNCS and PhNCO with diene replacement; however the only isolated product was $[Rh(CS)_2$ (formamidine)], to which a polymeric structure was assigned.

The reaction of $[Rh(CO)_2Cl]_2$ with Li{RNC(R´)NR} where (R´=H or Me) has been investigated by both Abel[125] and Connelly.[127] The complexes are thought to be binuclear bridged species, (Fig.1.10):



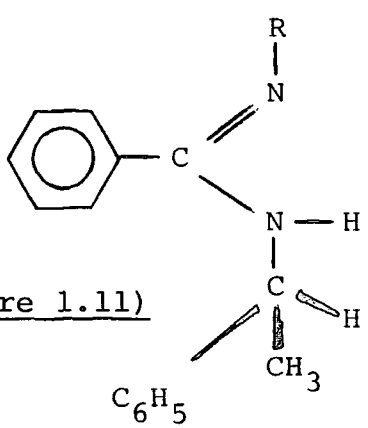
(Figure 1.10)

An intermediate, unstable and difficult to isolate was noted when R´=H. It is thought to be $Rh(CO)_3N(C_6H_4X)CH{:}N{-}(C_6H_4X)$ (X=F or Cl), which can easily lose CO to form the bridged dimers. $\{Rh(RNC(Me)NR)(CO_2)\}_2$ undergoes the reactions, (R=p-tolyl):



$[Rh(CO)L_2\{MeC(=NR)NHR\}][BF_4]$ has also been prepared directly from the appropriate diaryl acetamidine and $[Rh(CO)L_2(OCMe_2)][BF_4]$. ($L = PPh_3$) R=Ph or p-tolyl).[128]

As part of his studies in asymmetric catalysis, Brunner[129] found that $[RhCl(C_8H_{14})_2]_2$, together with the optically active amidines (i⟶v.) (Fig.1.11) or their lithium derivatives,



(Figure 1.11)

(i); R = $CH_2(C_6H_5)$

(ii); R = C_6H_5

(iii); R = $CH(CH_3)_2$

(iv); R = (S)$CH(CH_3)(C_6H_5)$

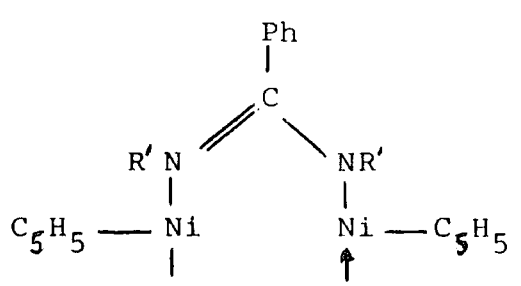
(v); R=(R)$CH(CH_3)(C_6H_5)$

produce catalysts after activation with molecular hydrogen. At room temperature and 1:1 bar H_2 pressure the catalysts hydrogenate the prochiral substrates (Z)-α (N-acetylamino)-cinnamic acid, itaconic acid, α-methylcinnamic alcohol, as well as cyclohexane, benzene, and toluene. However, the catalytic hydrogenation activity is balanced by low optical induction. Only the hydrogenation of α-methylcinnamic alcohol with 1.5-2.0% led to values different from zero.

Iridium complexes related to the complexes of rhodium described above have also been synthesised and analogous reactions investigated.[126,128]

Recently Piraino[130] reported that $[Rh(C_8H_{12})\{$p-tolyl N-C-(H)N-p-tolyl$\}]$ undergoes chemical oxidation by $AgNO_3$ leading to the paramagnetic $[Rh_2\{$p-tolylNC(H)N-p-tolyl$\}_3(NO_3)_2]$ (XI). Characterised by X-ray crystallography, the structure has a symmetrical arrangement of five ligand atoms around each rhodium atom, and a Rh-Rh distance of 2.485Å. The complex (XI) undergoes a variety of reactions. With nucleophilic agents displacement of the nitrato-groups occurs leading to complexes $[Rh_2\{$p-tolyl NC(H)N-p-tolyl$\}_3\text{-}X_2]$; $(X=I^-, SCN^-)$. The neutral ligands PPh_3 and pyridine were found to react slowly with (XI) yielding triphenylphosphine and pyridine oxide respectively. There is a corresponding yield of mixed valence formamidinate-complexes where the oxidation state of the rhodium atoms had been reduced.

(G) Ni, Pd, Pt: compared to other members of the group, nickel has received little attention. Treatment of $[(\eta^5\text{-Cp})Ni(PPh_3)Cl]$ with PhNC(Ph)N(Ph)Li afforded a brown, insoluble, involatile powder.[96] Analytical data indicated the formulation $[(Cp)Ni\{PhNC(Ph)NPh\}]$, and its instability and insolubility indicated a polymer. The i.r. spectrum indicates bridging amidino groups. A proposed structure, with retention of an 18-electron configuration for the nickel atom was given as (Fig.1.12):

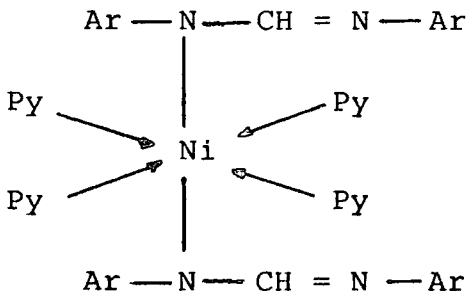


(Figure 1.12)

The complex was found to be very resistant to chemical attack, and clearly it differs fundamentally from the known monomeric

η-allyl derivative [Cp-Ni-Cp].[131]

A nickel, N,N´dinitrophenylformamidine tetrapyridine adduct has been synthesised by Bradley,[132] which was tentatively formulated as (Fig.1.13):



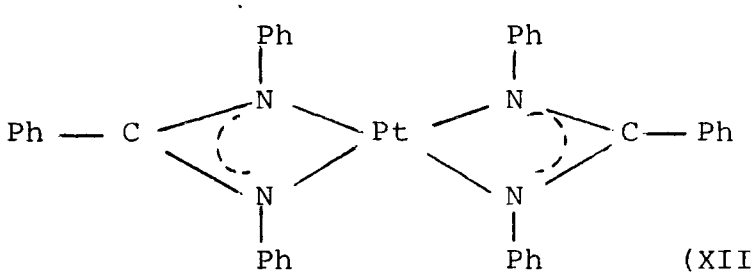
(Figure 1.13)

on the basis of analysis, molecular weight measurements and chemical reactivity.

In contrast it was platinum which provided the first amidine complexes. Usually they were formed to assist the analysis of amidines. The first complex was prepared by Limpricht[133] by the reaction of N,N diphenylbenzamidine hydrochloride with platinum chloride yielding a complex identified by Pinner[134] as $(RN.C(R').NHR.HCl)_2PtCl_4$. A number of similar platinum complexes were synthesised by the early workers.[135-140] Tschugaev[141] prepared a platinum nitrile complex in which the platinum was thought to bond to four ammonia molecules and two acetonitrile molecules. The anomalous coordination number of the platinum (II) in the complex, six or five, led to a number of studies[142-4], but it was only when Stephenson[145] determined the structures as diamimine-bis-(acetamidine)platinum (II) chloride monohydrate that the complex was finally shown to be $Pt(NH_3)\{CH_3C(NH_2).NH\}_2Cl_2H_2O$.

The reaction of amidines $\{R'N(X)C(R)NR'\}$, (X=H or Li), with platinum or palladium compounds results in the formation

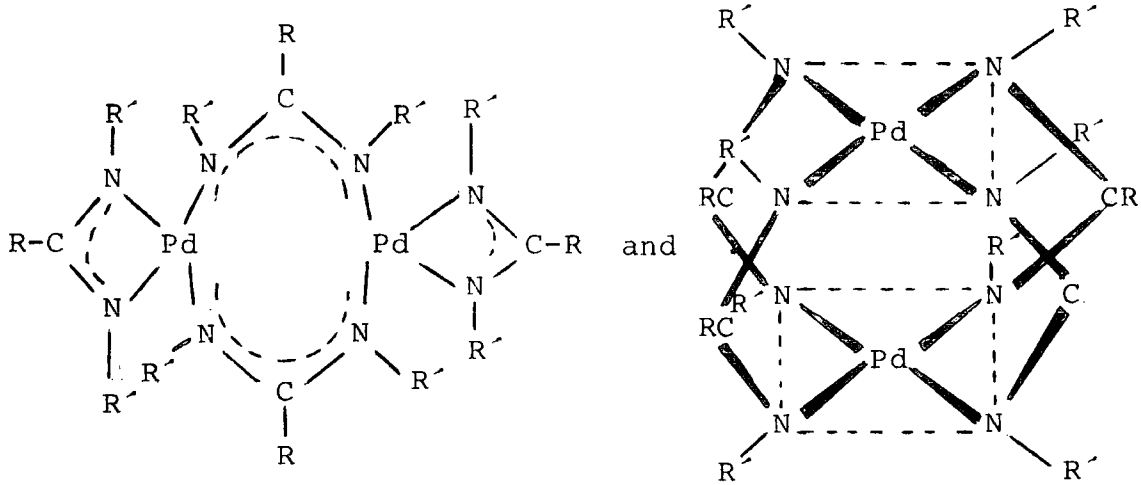
of a variety of complexes,[67,73,146-8] their nature depending on the amidine substituents, the metal, and the synthetic route used. This thesis is concerned in part with such complexes which will be described in detail in a later chapter. The reaction of $M(PhCN)_2Cl_2$ (M=Pt, Pd), with lithioamidines results in the formation of $Pt(Am)_2$, where Am = R´NC(R)NR´, and $Pd(Am)_2$ and $Pd_2(Am)_4$ complexes. The structure of $Pt(PhNC(Ph)NPh)_2$ has been determined,[67] (Fig.1.14):



(Figure 1.14)

(XII)

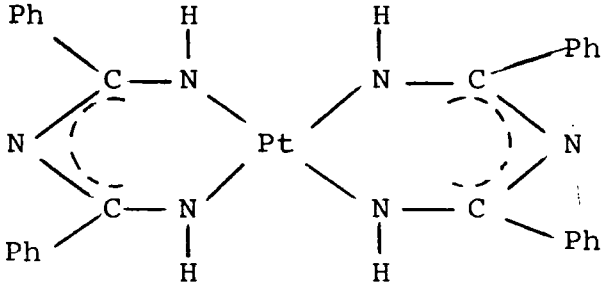
It is monomeric and analogous to carboxylate platinum bonding types. The palladium complexes have been shown to be dimeric in the case of formamidines (R=H) [146] by spectroscopic methods, monomeric and similar to (XII), in the acetamidine case ($R=CH_3$); by crystallography; and dimeric in the benzamidine case by spectroscopic methods. Possible dimer structures are (Fig.1.15):



(Figure 1.15)

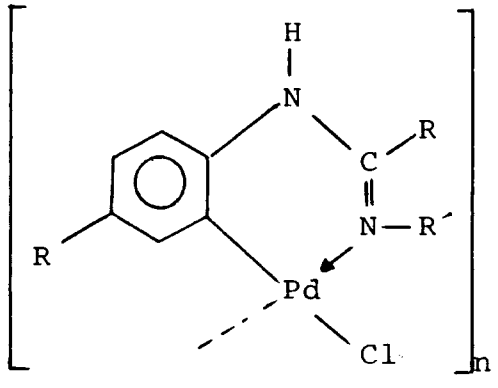
N.M.R. (^{19}F) studies have indicated fluxionality when M=Pd, R=C_6H_5, R´=C_6H_4 F-p).[147]

Treatment of $Pt(PhCN)_2Cl_2$ with $\{HN(Li)C_6H_5NH\}$ resulted in nucleophilic attack at the nitrile and formation of $Pt\{HNC(C_6H_5)NC(C_6H_5NH\}_2$, the structure was determined crystallographically (Fig.1.16):



(Figure 1.16)

With K_2MCl_4(M=Pt,Pd), N,N´diarylamidines form dark green *ortho*-metallated polymeric compounds (Fig.1.17):



(Figure 1.17)

The chloro-bridges can be cleaved by a variety of reagents, *e.g.* R´N Li(R)NR´, to form monomeric complexes.[73,148]

A number of "mixed" ligand amidine palladium complexes have been prepared and their properties studied. Vrieze[149] synthesised both η^3 (methylallylditolyl formamidino and acetamidino palladium complexes by two methods. By the reaction of two equivalents of silver amidine with $[(\eta^3RC_3H_4)PdCl]_2$ and by the reaction of amidine in the presence of KO-t-bu, with $[\eta^3RC_3H_4)PdCl]_2$.

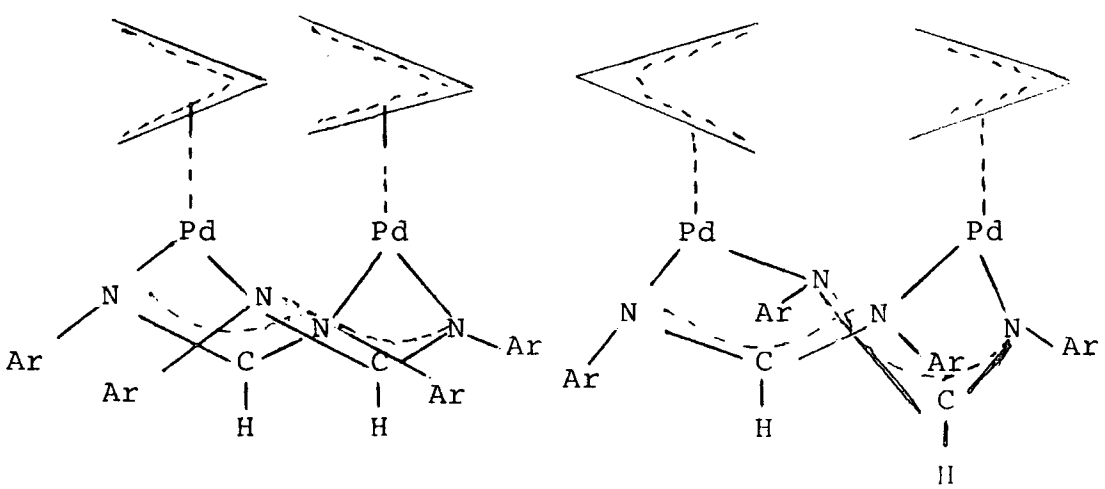
On the basis of molecular weight, spectroscopic properties, and analogy with the crystal structures of analogous triazene complexes, it was concluded that the complexes were dimeric with bridging amidine groups.

Toniolo, has undertaken similar studies using the following reactions:

(1) $[Pd(\eta^3\text{-allyl})Cl]_2 + 2Li[RNC(H)NR] \longrightarrow [Pd(\eta^3\text{-allyl})\{RN\text{-}C(H)NR\}]_2 + 2LiCl.$ [150]

(2) $[Pd(\eta^3\text{-allyl})Cl]_2 + 2[RN(H)C(H)NR] \longrightarrow 2PdCl[RN(H)C(H)NR](\eta^3\text{-allyl}).$ [151]

The first reaction produces a mixture of non-interconverting isomers (Fig.1.18):



(Figure 1.18)

The conformer which has two equivalent allyl groups was found to have their concentration ratio independent of temperature, suggesting that no intramolecular processes take place. The other conformer at 80-100°C undergoes an intramolecular process which results in the equivalence of the allyl groups. The presence of bridge-splitting ligands such as dimethylsulphoxide or N,N´diarylformamidines, does not affect the intramolecular process, which thus occurs without any palladium-

formamidides bond breaking, possibly through a broad inversion of the $C_2N_4Pd_2$ ring *via* a chair conformation.

The second reaction involves bridge splitting and the products show fluxionality which was studied by variable temperature ^1H and ^{13}C N.M.R. Two dynamic processes were thought to occur (Fig.1.19). The first operating at room temperature involved the dissociation of the neutral amidine ligand (a), the second which has a lower activation energy, was found to be concentration dependent and involves chloride amidine exchange, thought to be *via* a penta coordinated chloro-bridged species, (b).

(a)

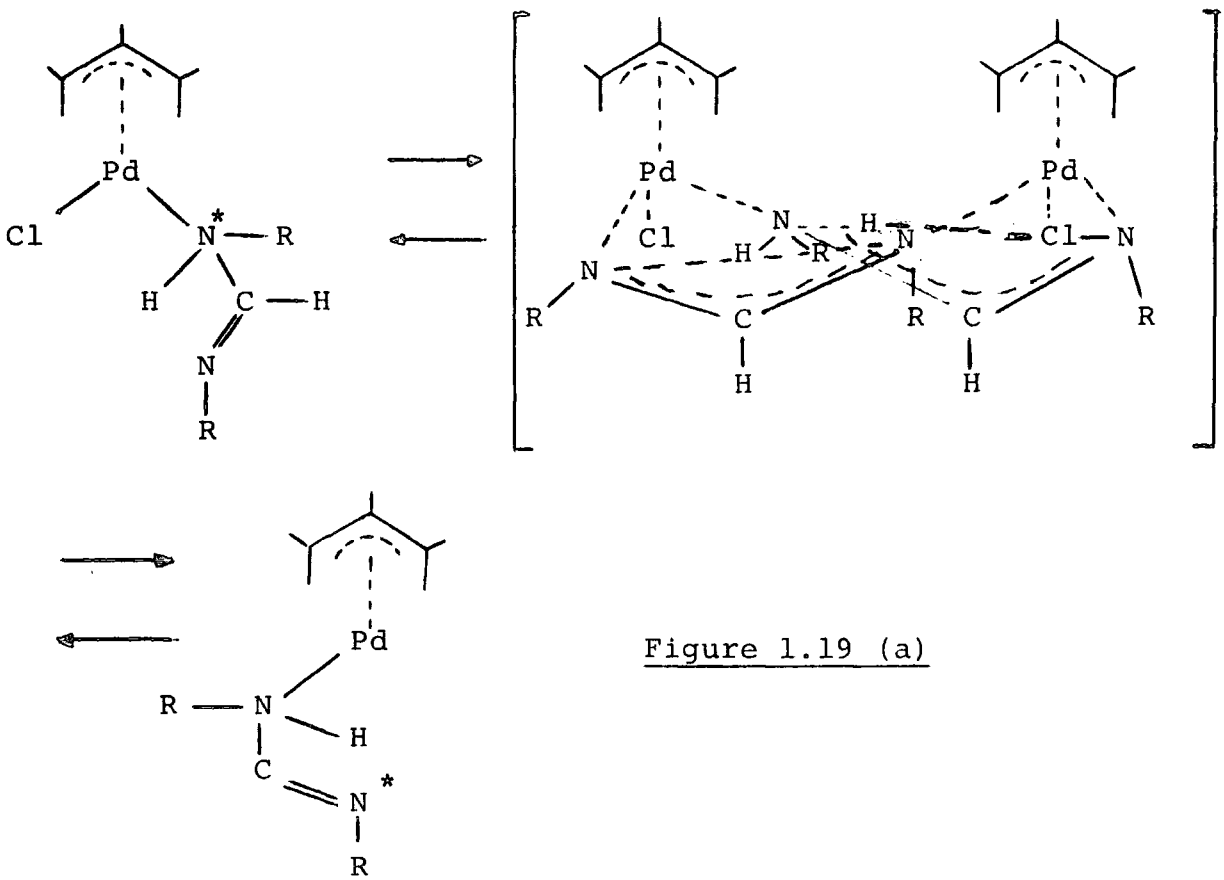
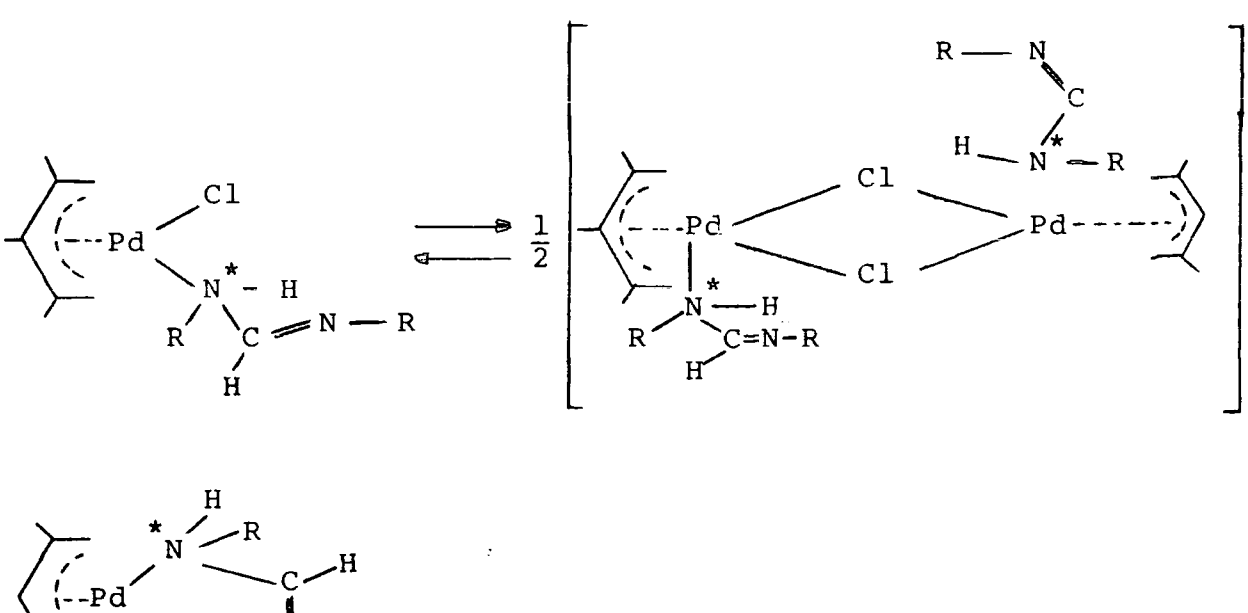


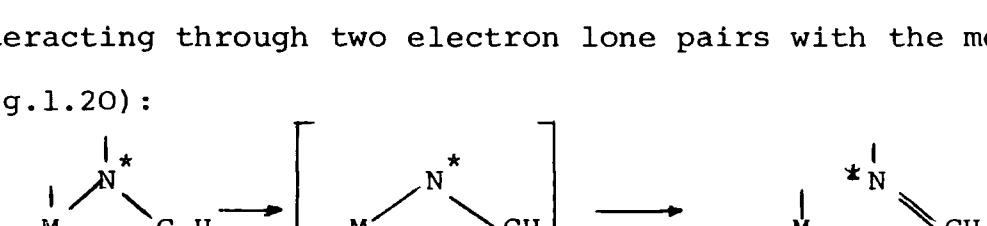
Figure 1.19 (a)

Interestingly the mechanism indicates amino-nitrogen-metal bonding when imino-nitrogen-metal bonding is more likely.



(Figure 1.19)(b)

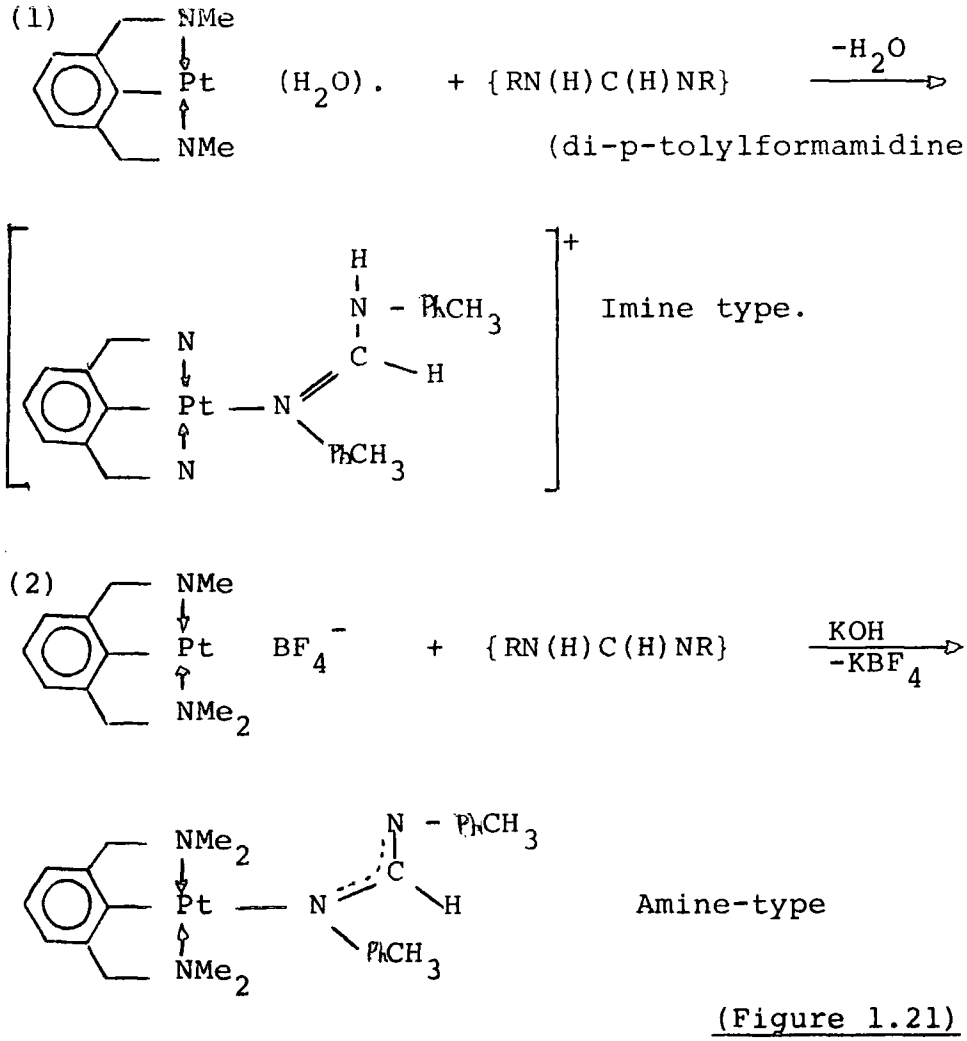
For complexes of the type $M(PPh_3)_2Cl(RNC(H)NR)$ (where M=Pt or Pd), proton N.M.R. variable temperature studies show a fluxional behaviour which has been interpreted as occurring *via* a penta coordinated intermediate with both nitrogen atoms interacting through two electron lone pairs with the metal,[146,152] (Fig.1.20):



(Figure 1.20)

The complexes were synthesised by the reaction of $M(PPh_3)_2Cl_2$ with lithioamidines.

Vrieze[65] has synthesised some monomeric amidine complexes using the following routes (Fig.1.21):

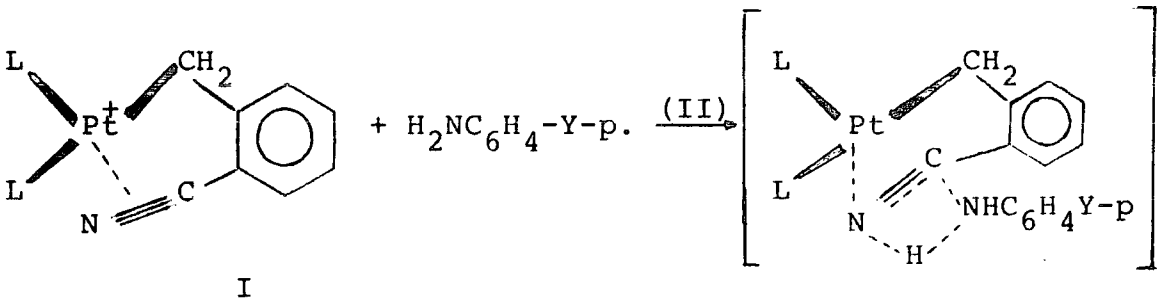


(Figure 1.21)

Similar palladium species have been synthesised and in solution the neutral palladium species are fluxional, N.M.R. indicating that a chelating unit exists.

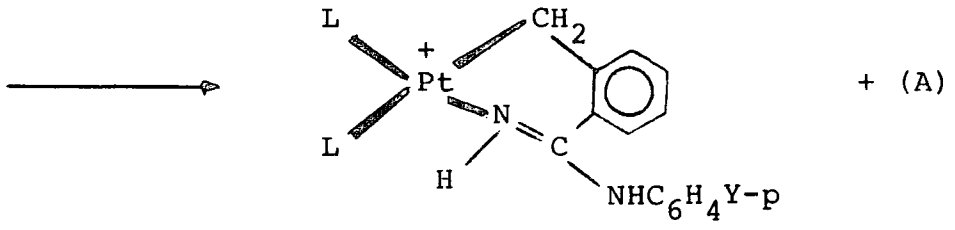
The mechanism of formation of amidine complexes by the reaction of the dimeric *O*-cyanobenzyl complex cis-$[Pt(O\text{-}CH_2\text{-}C_6H_4CN)(PPh_3)_2]_2(BF_4)_2$ with primary anilines has been investigated.[153] The first stage of this two phase proces is thought to involve displacement of the nitrile group by the entering amine leading to a labile mononuclear amine complex bearing a pendant-CN group. The second slower stage is thought to involve the intermediate reacting with the amine *via* attack

of the amine nitrogen on the nitrile carbon to yield the platinum (II) amidino-species (Fig.1.22):



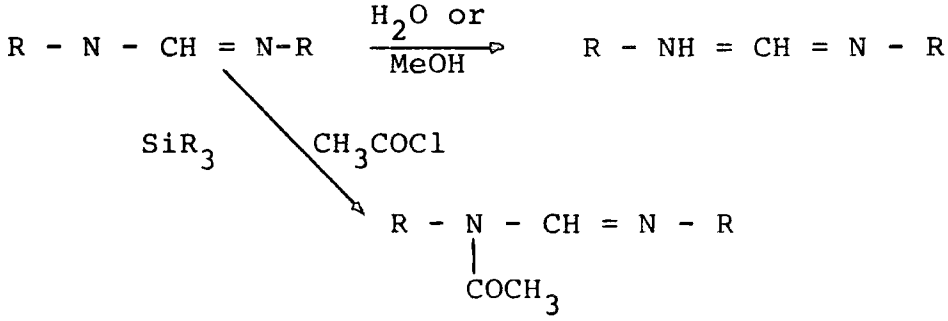
I

(Figure 1.22)

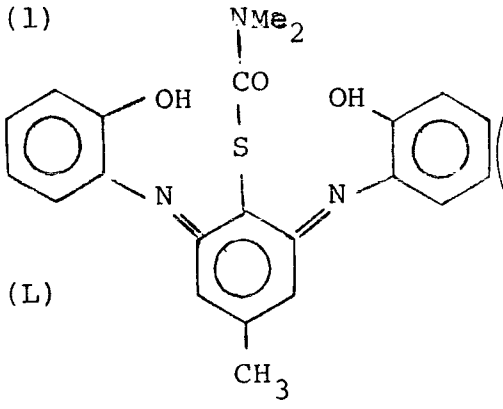


(Y - p-OMe p-Me H).

A further reaction of note is that in the presence of catalytic amounts of palladium chloride or tri(triphenylphosphine)chlororhodium, the hydrosilation of carbodiimides occurs to form N-silylformamidines in high yield.[154] The synthetic value of the products was shown by the following reaction:



Robson[155-6] has used amidines as a bridging ligand in studies of palladium (II) complexes containing binucleating ligands (Fig.1.23):

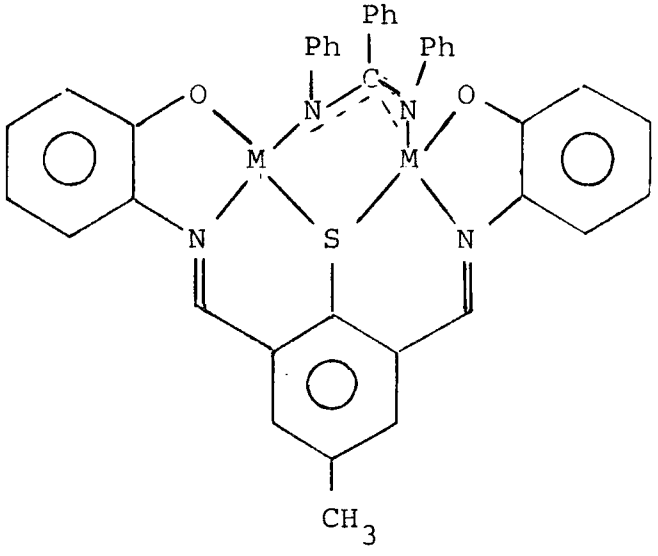
(1) 

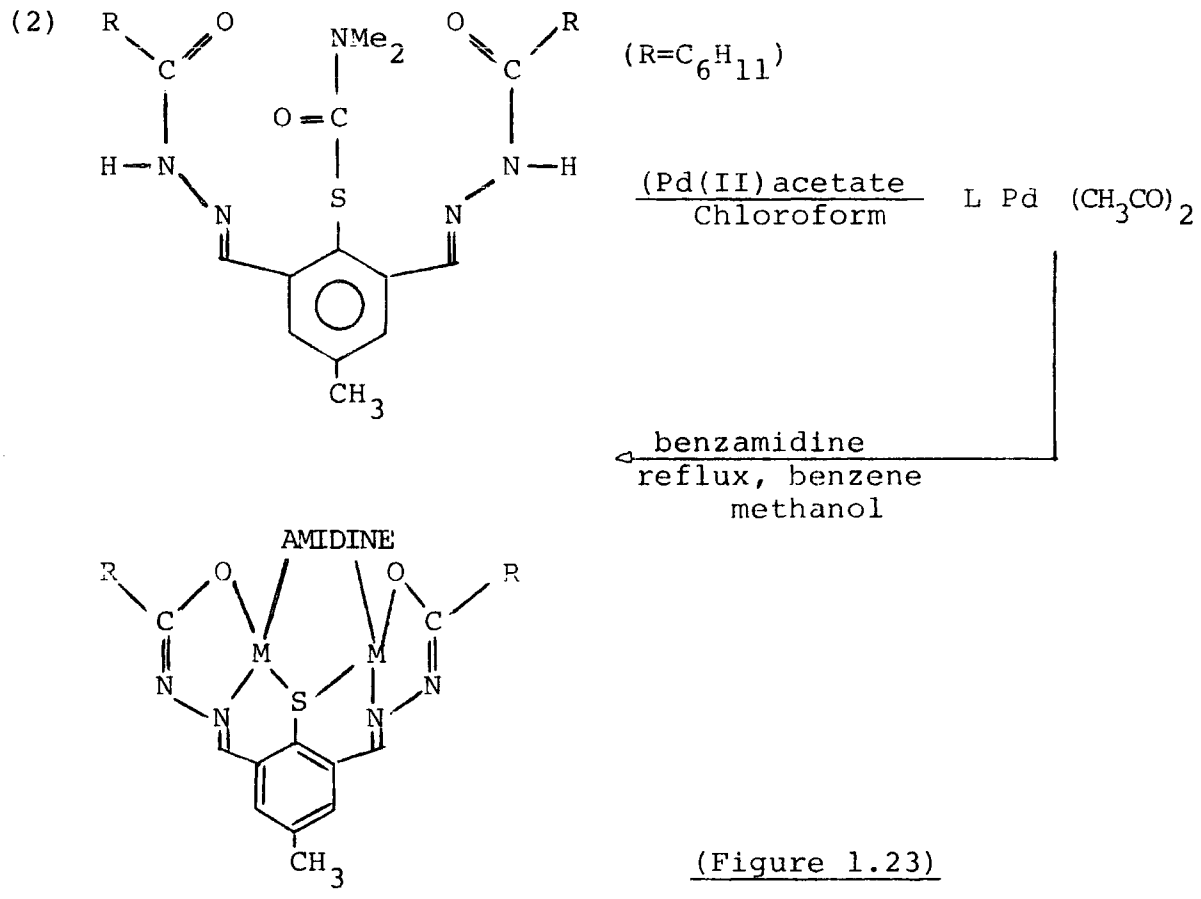
2-Mercapto-5-methylisophthaldehyde di-2 -hydroxyanalil

(L) + Pd(II) acetate

$\xrightarrow{CHCl_3}$ L Pd $(CH_3\ CO)_2$. $CHCl_3$ + one other unidentified product.

L. Pd $(CH_3CO)_2 . CHCl_3$ + N,N′diphenyl benzamidine ("bridge substitution reaction"). ⟶



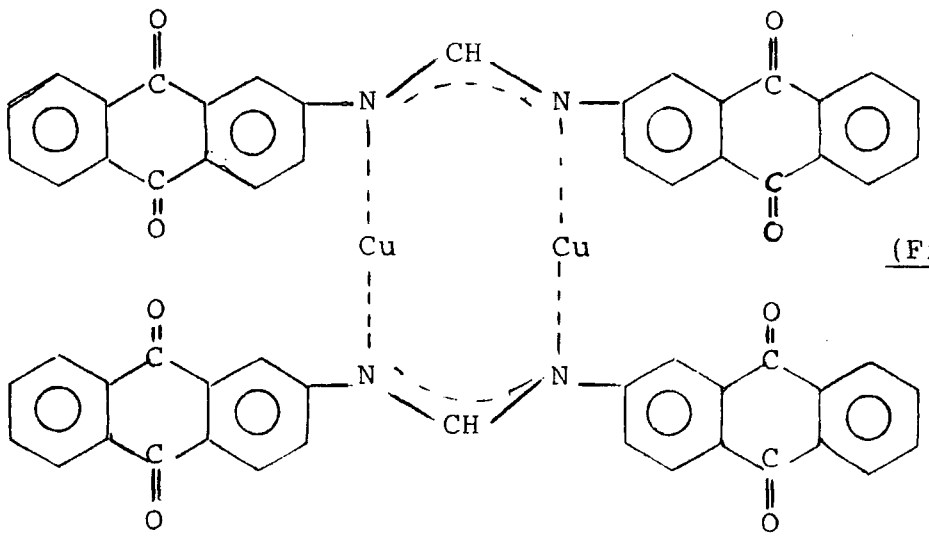


(Figure 1.23)

The complexes were prepared to build up procedures for a generation of complexes containing a wide range of pairs of "soft" metal centres. Such complexes are of interest because of the possibilities they offer for new types of reaction at the bridging sites such as those occupied by the amidines.

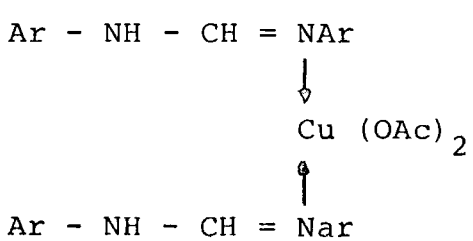
(H) Cu and Ag: Copper and silver, like platinum were studied early in the history of transition metal amidine chemistry. Pinner,[134] used silver complexes in a similar manner to those of platinum to analyse amidines, and Bradley synthesised a

number of copper and silver N,N'diarylamidine complexes.[132,157] The copper complexes of N,N'di-anthroquinonyl formamidine or benzamidine were tentatively assigned the following structure (Fig.1.24):



(Figure 1.24)

on the basis of its high solubility and chemical inertness, and hence a high degree of covalency between the copper and nitrogen atoms. The compound was later found to be tetrameric. It was formed from the reactions of cuprous chloride, cupric acetate or copper bronze with N,N'-di-2-anthraquinonyl formamidine. The isomeric N,N'-1-anthraquinonylformamidines do not yield the corresponding copper complexes. A number of green, unstable cupric N,N'-diarylformamidines were also synthesised and tentatively assigned the structure (Fig.1.25):



(Figure 1.25)

on the basis of molecular weight measurements and chemical activity.

An acetamidinium tetrachlorocuprate[129,158-9] complex analogous to the cobalt complex mentioned previously,[120] has also been synthesised. It was characterised by X-ray crystallography, optical spectra and E.P.R. spectra. A structural model was proposed in which $CuCl_4^{2-}$ layers were separated by acetamidinium ions; the $CuCl_4^{2-}$ ions alternately occupying tetragonal and tetrahedral sites.

Carboxylato-analogue Copper (I) and Copper (II) amidine complexes have been investigated by Kilner.[160-1] Lithioamidines $\{R'N(Li)C(R)NR'\}$ (R=H, CH, C_6H_5i $R'=C_6H_5$, p-$CH_3C_6H_4$) react with anhydrous copper (II) chloride to form $[Cu\{R'NC(R)NR'\}_2]_n$ complexes, and with anhydrous copper (I) chloride to form $Cu\{R'NC(R)NR'\}]_m$. The Cu(II) complexes are air stable in the solid state and diamagnetic. Experimental data indicated a dimeric structure, which was proven by X-ray crystallography.[161] The structure has four bridging amidine groups and a short Cu-Cu distance (2.46Å). The Cu(I) complexes are less stable decomposing rapidly in air when in solution. The complexes reacted in the following manner:

(1) $Cu\{PhNC(CH_3)NPh\}_2$ + Pyridine ⟶ $Cu\{PhNC(CH_3)NPh\}_2$ Pyridine

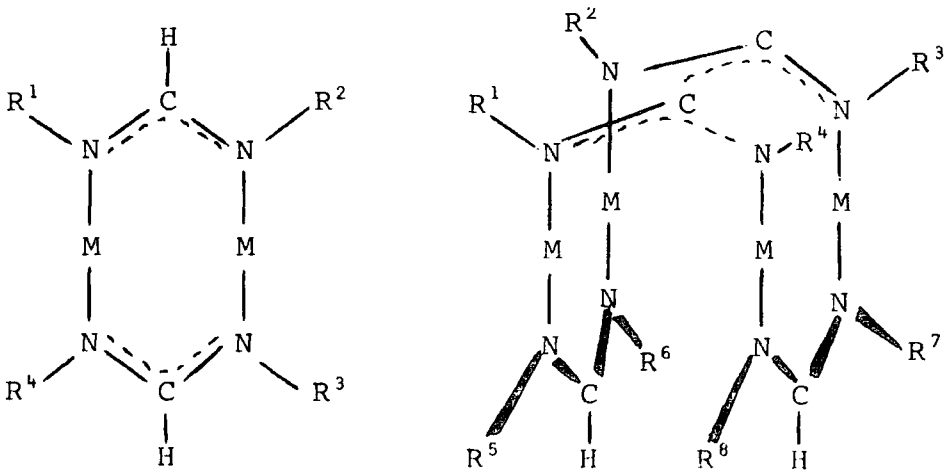
(2) $Cu\{PHNC(CH_3)NPh\}_2 + CS_2 \longrightarrow Cu\{PhNC(CH_3)NPh\}_2\ CS_2$

$\longrightarrow Cu\{PhNC(CH_3)NPh\}CS_2$

Interestingly, thermogravimetric analysis indicates that thermal decomposition does not occur in simple ligand loss steps as might be expected from its structure but may involve complicated "internal" species. In solution the Cu(I) complexes vary in the degree of disproportionation to Cu^{O} and Cu^{II} stability decreasing from formamidines to acetamidines to

benzamadine complexes. Solutions of formamidine complexes show hardly any sign of disproportionation and a detailed study of dimer-dimer and dimer-tetramer equilibria for these complexes has been carried out by Vrieze.[162]

A number of copper and silver formamidine complexes $[M\{RNC(H)NR\}_n$ (R=p-tolyl; R $=CH_3$, C_2H_5, i-propyl, t-butyl, C_6H_{11}, n=2,4), were prepared and studied by ^1H and ^{13}C N.M.R., as a function of temperature, concentration, metal atom, and alkyl substituent. The studies show the presence of dimeric and tetrameric isomers (Figure 1.26):



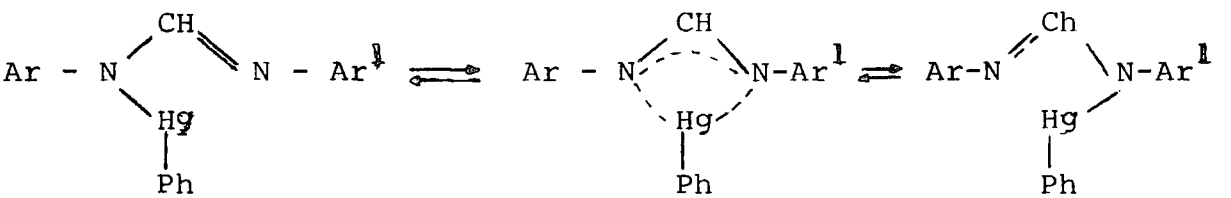
(R = alkyl or p-tolyl)

(Figure 1.26)

It requires only one metal-nitrogen bond in each dimer to be broken and two new metal-nitrogen bonds to be formed to give four tetrameric isomers. Conclusions from the studies were: (1) the size of the alkyl substituents determines the relative ratios of the tetramers, (2) increasing temperatures cause a corresponding dimer/tetramer ratio increase, (3) increasing bulk of alkyl substituents cause a corresponding increase in the dimer/tetramer ratio, and (4) the dimer/tetramer ratio is increased when silver (I) is replaced by copper (I).

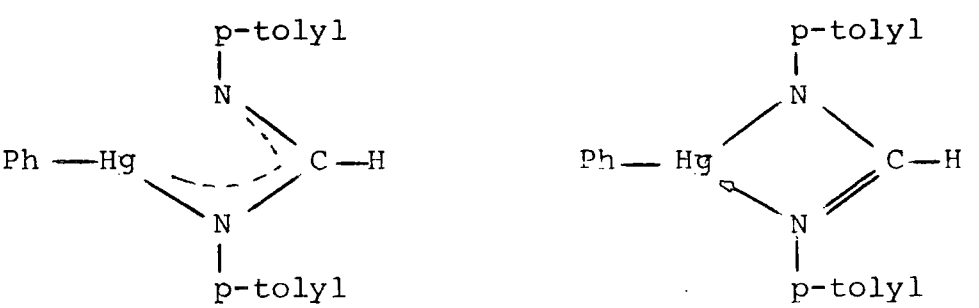
(I) Zn, Cd, and Hg: a number of complexes of the type (Amidine)$_2$ MX_2 (M=Zn, Cd, Hg; X=Br, Cl) have already been described under cobalt.[121]

The reaction of equimolar quantities of phenylmercury hydroxide and N,N´diarylamidines in ethanol yielded complexes of the type PhHg{PhNC(H)NPh}.[66] N.M.R. studies indicate that the following equilibrium occurs (Fig.1.27):



(Figure 1.27)

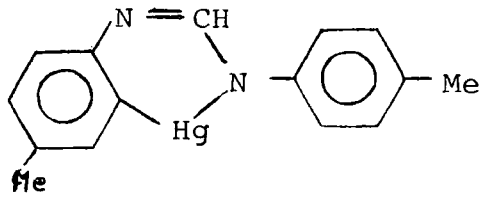
and an X-ray determination of PhHg(p-tolyl NC(H)N-p-tolyl) complex showed two independent molecules to be present. One is a monodentate complex (a),(Figure 1.28), the other a chelate (b), which is more evidence for the above equilibrium.



(a) (b)

(Figure 1.28)

One of the earliest *O*-metallated complexes known was formed by the reaction of mercuric acetate with, N,N´di-p-tolylformamidine.[132] The structure (Fig.1.29) was assigned on the basis of the complexes reaction with iodine to give N-(2-iodo-4-methyl phenyl)-N´-phenylformamidine.



(Figure 1.29)

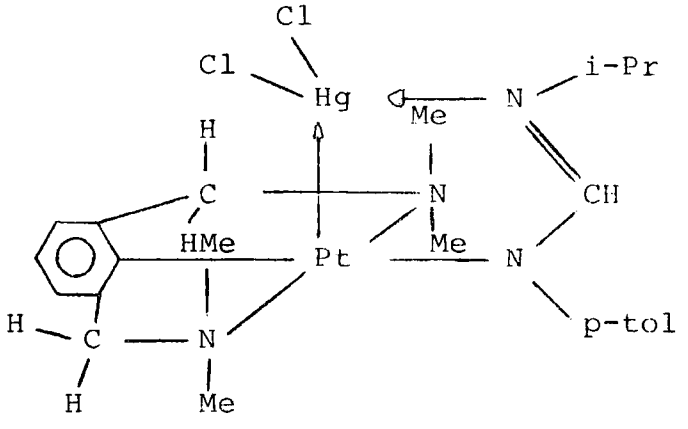
(J) Mixed-Metal Amidine Complexes: dinuclear complexes containing a metal-metal bond form a logical connection between mononuclear complexes, and compounds with linear stacks, clusters, and ultimately pure metal. Amidines have proved to be an excellent tool for studying mixed-metal-dinuclear compounds, and they have been extensively studied by Vrieze.

Complexes of the type [(diene){RNC(Y)NR}$_2$ RhHgCl], (diene= 1,5,cyclooctadiene, norbornadiene, Y=H, R=R´=Pr^i, R=CH_3, Pr^i, p-$CH_3C_6H_4$; R´=p-$CH_3C_6H_4$ and Y=CH_3, R=R´-p-$CH_3C_6H_4$), were prepared from the reaction of [(diene)RhCl]$_2$ with Hg{RNC(Y)NR}$_2$.[163] N.M.R. data indicates that the molecule consists of a rhodium atom coordinated by a bidentate amidino group, a HgCl ligand and a nitrogen-atom of an amidino group, which bridges the rhodium-mercury bond. ^{13}C N.M.R. indicated that for R =p-$CH_3C_6H_4$, the complexes are fluxional involving an interchange of the bridging and the chelating amidino groups *via* monodentate intermediates.

[$(PPh_3)_2$(CO)IrCl] reacts with [M.RNC(H)NR´]$_n$ (M=Cu, Ag; R-Me, i-Pr, t-Bu, cyclohexyl; R´=p-tolyl; n=2,4) to yield

$[(PPh_3)_2(CO)IrM\{RNCHNR'\}]$ complexes, in which there is a formal Ir-M bond which is stabilised by a bridging formamidino group.[164] The ease of formation and stability of the complexes was found to be $Ir^I > Rh^I$; $Ag^I > Cu^I$, and small R groups > large R groups. The bulk of the substituent R groups on the amidino nitrogens was found to influence which nitrogen bonded to a particular metal. Varying the bulk of one of these R substituents showed that when this NR group was small in bulk it bonded to either iridium or silver, thus producing two isomers. When R was high in bulk the NR group only bonded to the silver because of the influence of the two phosphine ligands on iridium. The corresponding rhodium compounds could not be isolated.

Complexes $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}$(p-tolyl NCHNR) Pt Hg Br Cl] (R=Me, Et, i-Pr) were prepared by Vrieze,[165] by the reaction of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}$-Pt Br] with [Hg(p-tolyl NCHNR) Cl], or in lower yield from the exchange reactions of $[\{2,6\text{-}(MeNCH_2)_2C_6H_3\}(RCO_2)$-Pt Hg CO_2(R)Br] with p-tolyl NC(H)N(H)Et. One of the complexes $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}$Pt (μ-{p-tolyl-NCH-N Pr^i}) Hg Br Cl] has been characterised crystallographically (Fig.1.30):



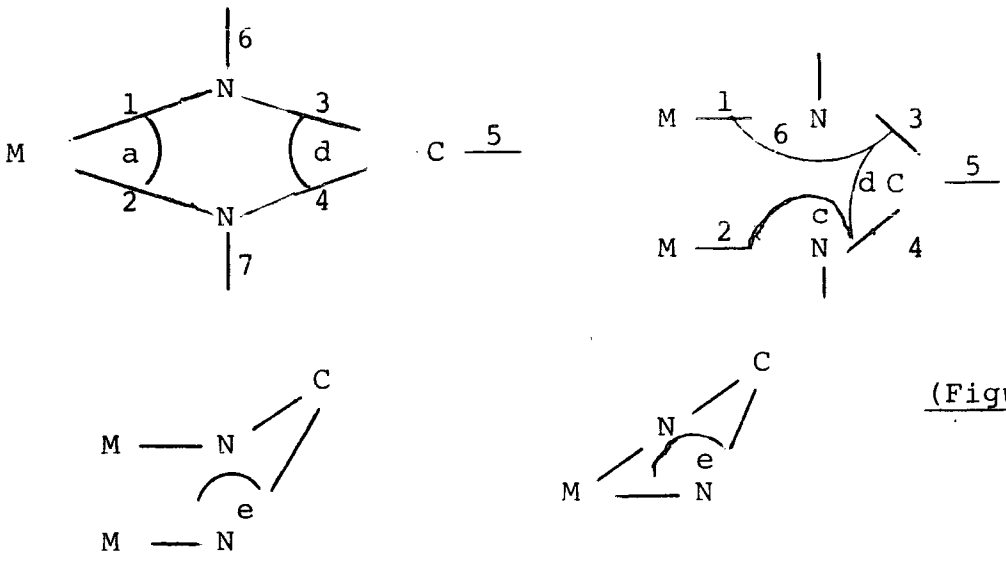
(Figure 1.30)

The five-membered ring is thought to act as a stabilising factor. The absence of a subsequent electron transfer reaction is thought to be due to the constraints of the terdentate $2,6(Me_2NCH_2)_2C_6H_3$ ligand, which fixes the N-donor atoms in mutual trans-positions. The Pt to Hg interaction in the amidine case is described as a donor type ($Pt \xrightarrow{x} Hg$) in contrast to that found for $[(2\text{-}Me_2NCH_2C_6H_4)_2(MeCO_2)\text{-}PtHg\text{-}(O_2CMe)]$ which is a standard covalent interaction ($Pt \overset{x}{-} Hg$).[166]

The terdentate $2,6(Me_2NCH_2)_2C_6H_3$] ligand has also been used to stabilise platinum to silver bonds. The complexes {[2,6-$(Me_2NCH_2)_2C_6H_3$](p-tol NCHNR}Pt Ag Br}, (R=Me, Et, i-Pr R-p-tolyl) are formed from the reaction of {[2,6-$(Me_2NCH_2)_2C_6H_3$] Pt Br} with $[Ag\{p\text{-tol NC(H)NR}\}]_n$.[167] The complexes are thought to involve a five-membered chelate ring in which a Pt (II)-Ag(I) bond is bridged by a formamidino ligand. The complex was studied by INEPT ^{109}Ag N.M.R.,[168] which supported the proton N.M.R. conclusions that there are two isomers present. The dependence of the isomer ratio on the alkyl substituent was also noted.

1.5 X-Ray Structures of Amidine Complexes

The bond lengths, and angles reported in Table 1.2 and discussed below will be based on the following key (Fig.1.31):



(Figure 1.31)

e is a dihedral angle.

Note, angle "e" is a measure of the non-planarity of the amidine-metal ring. In some cases a qualitative description only can be given.

Although standard deviations, crystal packing factors, and trans effects all influence the structural parameters listed in Table 1.2, a number of generalisations can be made.

One of the most important structural parameters is the N-C-N "bite" angle. In the chelate (Fig.1.3) complexes it appears to be affected by the substituent group on the amidine. For formamidine, an average value of 115^{o} is found, for acetamidine 108^{o}, and for benzamidine 110^{o}. Thus N-C-N decreases in the complexes in the following manner: formamidine >benzamidine>acetamidine. These values may be compared with the average chelate triazene value for the N-N-N angle of 103^{o}.[176]

COMPOUND (Ref.)	BOND LENGTH								BOND ANGLES				
	Structure	1	2	3	4	5	6	7	A	B	C	D	E
$TaMeCl_2\{C_6H_{11}NC(Me)NC_6H_{11}\}_2$ (monoclinic[68]	Fig. (Fig. 1.3) c,b	2.160(17)	2.040(17)	1.37 (3)	1.39 (3)	1.48 (3)	1.49 (3)	1.43 (3)	61.9(38)	95.9(12)	95.9(13)	106.2(13)	"planar"
		2.149(19)	2.187(17)	1.40 (3)	1.27 (3)	1.50 (3)	1.50 (3)	1.53 (3)	60.4(58)	95.6(13)	98.1(12)	105.8(17)	
$TaCl_3\{C_3H_7NC(Me)NC_3H_7\}_2$ (monoclinic).[169]	c,b	2.098(14)	2.193(16)	1.36 (3)	1.36 (3)	1.54 (3)	1.43 (3)	1.43 (3)	62.4 (6)	96.2(11)	92.0(12)	109.4(16)	"planar"
		2.058(15)	2.180(20)	1.36 (3)	1.32 (3)	1.55 (3)	1.49 (3)	1.49 (3)	60.1 (7)	99.4(14)	95.1(14)	105.4(20	
$TaCl_3\{C_3H_7NC(Me)NC_3H_7\}_2$ (orthohombic-two independent molecules opposite enantiomorphs (I) and (II).[170]	(I) c,b	2.182(20	2.176(23)	1.35 (4)	1.33 (3)	1.56 (4)	1.45 (4)	1.38 (4)	61.9 (9)	91.9(16)	92.7(17)	113.4(24)	"planar"
	(II)	2.114(19)	2.209(21)	1.32 (3)	1.30 (3)	1.52 (4)	1.38 (4)	1.44 (5)	58.6 (8)	98.3(16)	93.2(16)	109.1(22)	
		2.122(18)	2.171(22)	1.27 (3)	1.35 (3)	1.46 (4)	1.51 (4)	1.54 (4)	59.3 (8)	99.9(15)	95.0(16)	106.4(21)	
		2.135(18)	2.223(20)	1.25 (3)	1.41 (3)	1.50 (4)	1.54 (4)	1.47 (4)	59.8 (8)	94.8 (15)	95.7(17)	109.6(23)	
$TaCl_3\{C_6H_{11}NC(Me)C_6H_{11}\}_2$ (tetragonal) (171)	c,b	2.168(19)	2.159(19)	1.34 (4)	1.40 (4)	1.51 (5)	-	-	61.7 (8)	95.7(19)	94.2(15)	108.3(24)	"planar"
		2.089(22)	2.158(23)	1.33 (4)	1.33 (4)	1.56 (5)	-	-	61.6 (9)	96.1(18)	93.0(18)	109.2(27)	
$TaCl_3\{C_6H_{11}NC(Me)NC_6H_{11}\}\{C_6H_{11}NC(NHC_6H_{11})O\}$. (monoclinic).[171]	c	2.148(19)	2.112(18)	1.30 (3)	1.28 (3)	1.57 (3)	-	-	59.8 (8)	92.6(15)	94.8(15)	111.2(18)	"planar"

TABLE 1.2 STRUCTURAL PARAMETERS

COMPOUND (Ref.)	Structure	BOND LENGTH 1	2	3	4	5	6	7	BOND ANGLES A	B	C	D	E
$TaMeCl_2\{C_3H_7-N-C$	c	2.174(22)	2.073(24)	1.39 (4)	1.23 (4)	1.56 (5)	-	-	59.7 (9)	91.3(13)	101.1(20)	107.8(27)	"planar"
$Me)N-C_3H_7\}_2C_6H_6$		2.112(20)	2.226(19)	1.43 (4)	1.26 (4)	1.56 (4)	-	-	61.9 (8)	93.1(16)	92.9(17)	112.2(25)	
(monodinic)[172]													
$Cr_2\{CH_3NC(Ph)N$	f	2.025 (5)	2.024 (5)	1.332(7)	1.318(7)	1.496(7)	1.471(7)	1.472(7)	-	115.7 (4)	115.9 (4)	116.5 (5)	"planar"
$CH_3\}_4$.[90]		2.036 (4)	2.043 (5)	1.351 (7)	1.339 (7)	1.467 (8)	1.458 (7)	1.450 (7)	-	115.5 (3)	115.9 (4)	116.1 (5)	
$Mo_2\{2,6$ xylyl NC	f	2.156 (5)	2.167 (5)	1.337 (7)	1.333 (7)	1.523 (8)	1.443 (7)	1.456 (7)	-	119.1 (4)	118.9 (4)	117.4 (5)	"planar"
$(CH_3(2,6$ xylyl$\}_2$													
$(CH_3CO_2)_2$4.													
C_4H_8O.[91]													
$Mo_2\{PhNC(CH_3)N$	f	2.161 (5)	2.160 (5)	1.342 (7)	1.329 (9)	1.520 (9)	1.425 (7)	1.428 (7)	-	119.3 (4)	119.3 (4)	116.1 (5)	"planar"
$Ph\}_3(CH_3CO_2)$.[91]		2.151 (5)	2.115 (4)	1.321 (7)	1.388 (7)	1.541 (8)	1.441 (7)	1.421 (8)	-	118.4 (4)	119.8 (4)	116.1 (5)	
		2.140 (5)	2.132 (5)	1.360 (7)	1.340 (7)	1.512 (8)	1.418 (7)	1.418 (7)	-	119.6 (4)	120.1 (4)	115.0 (6)	
$Mo(CO)_2\pi-C_5H_5$	b	2.176 (3)	2.169 (3)	1.320 (4)	1.320 (4)	1.499 (5)	1.416 (4)	1.407 (4)	53.9 (1)	96.4 (2)	96.7 (2)	108.0 (5)	"planar"
$\{PhNC(CH)_3NPh\}$.[98]													
$Mo(CO)_2(R''-C_5H_4)$	(I)a)	2.175 (7)	2.199 (6)	1.310(11)	1.295(11)	1.52 (1)	1.440 (4)	1.453(10)	59.2 (2)	94.4 (5)	93.4 (5)	112.8 (8)	3.38
$\{(HCPhR)-N(CPh)-N-$	b)	2.173 (6)	2.190 (7)	1.310(10)	1.303 (9)	1.50 (1)	1.458 (9)	1.474 (9)	59.0 (2)	95.4 (5)	94.9 (5)	110.6 (6)	2.01
$(HCPhR')\}$. (I),													
$R''=R'=H$, $R=CH_3$)													
(II), $R''=R'-H$,	(II)	2.149 (6)	2.177 (6)	1.299 (9)	1.291 (9)	1.43 (1)	1.461 (9)	1.460 (8)	58.8 (2)	96.1 (5)	95.0 (5)	110.1 (7)	1.14
$R-CH_3$ difference													
only in the con-													
formation at the													

TABLE 1.2 (contd.-2)

COMPOUND (Ref.)	BOND LENGTH								BOND ANGLES				
	Structure	1	2	3	4	5	6	7	A	B	C	D	E
C-CH(CH_3)Ph) substituent at the benzamidine ligand. (III), R´´-H, R´=R-CH_3 differs from I and II in that both nitrogens of the benzamidine ligand bear optically active substituents of composition (C-CH-(CH_3)-Ph). (IV), R´´=R´=CH_3 and it has optically active substituents at both benzamidine ligand nitrogens. Note Ia, Ib - two independent molecules in the asymmetric unit.[99]	(III)	2.186 (7)	2.134 (7)	1.323 (9)	1.365 (9)	1.48 (10)	1.466(10)	1.467(10)	60.7 (2)	94.7 (6)	95.8 (5)	108.5 (8)	5.70
	(IV) (b)	2.187 (6)	2.148 (5)	1.322 (8)	1.310 (9)	1.491 (8)	1.466 (9)	1.478 (8)	59.7 (2)	94.0 (5)	96.2 (4)	110.0 (7)	2.65

TABLE 1.2 (contd.-3)

COMPOUND (Ref.)	Structure	BOND LENGTH 1	2	3	4	5	6	7	BOND ANGLES A	B	C	D	E
$Mo_2\{PhNC(Ph)NPh\}_4$	f	2.125(9)	2.149 (5)	1.32 (1)	1.36 (1)	1.56 (2)	1.45 (1)	1.44 (1)	-	118.6 (5)	117.2 (5)	118 (1))	"plan
(69)		2.163(10)	2.149 (5)	1.38 (1)	1.33 (1)	1.37 (2)	1.43 (1)	1.44 (1)	-	119.9 (8)	118.3 (4)	114 (1)	ar"
$W_2\{PhNC(CH_3)NPn\}_2(C_6N_2OH_7)_2 \cdot 2C_4H_8O$. (92).	f	2.11 (1)	2.11 (1)	1.32 (2)	1.40 (2)	1.53 (2)	1.48 (2)	1.40 (2)	-	118. (1)	123. (1)	115. (1)	"plan-ar"
cgdh-di-μ-(N,N-di-3,5-xylformamidino)-e,f-di-μ-carbonyl-ab-(N,N´-di-3,5-xylyl formamidino)-ij-N^1 methylene-N1-3,5-xylyl-N^2-3,5-xylylformamidino-N^2,C)-W_2.[72]	f and	2.13 (3)	2.12 (3)	1.33 (5)	1.32 (5)	-	1.44 (5)	1.42 (4)	-	120. (3)	120. (2)	124. (3)}	"plan-ar"
		2.13 (3)	2.12 (3)	1.32 (5)	1.34 (4)	-	1.42 (4)	1.50 (5)	-	122. (2)	123. (3)	120. (3)}	
	b and i.	2.26 (3)	2.31 (3)	1.28 (5)	1.28 (3)	-	1.43 (5)	1.29 (4)	57. (1)	93. (3)	91. (2)	119. (4)	"planar"
		1.45 (6) $-CH_2-$ 2.26 (5)	2.20 (3)	1.32 (5)	1.36 (6)	-	1.47 (6)	1.41 (4)	78. (1)	107. (3) ($N-CH_2-W$)	110. (2)	123. (4)	"planar"
$Re_2\{PhNC(CH_3)NPh\}_2Cl_4$	f	2.08 (2)	2.08 (2)	1.31 (1)	1.37 (2)	1.53 (3)	1.43 (3)	1.43 (2)	-	119.8(14)	118.6(14)	118.5(20)	
(112)		2.02 (1)	2.07 (2)	1.37 (2)	1.36 (2)	1.51 (3)	1.50 (2)	1.43 (2)	-	121.1(13)	119.7(14)	115.2(18)	
$Re(PPh_3)_2(CO)_2(PhNC(H)NPh)$.[173]	b	2.22 (1)	2.22 (1)	1.32 (1)	1.34 (1)	-	1.41 (2)	1.39 (2)	60.0 (1)	94. (1)	94. (1)	112. (1)	"nearly planar"
$Re(CO)_4(CH_3CO)_2\{PhC(NH_2)_2\}$.[77]		-	-	1.301(7)	1.314(7)	1.488(9)	1.04 (10) 0.9 (2)	1.02 (7) 0.95 (9)	-	-	-	122.8 (7)	"amidine planar"

TABLE 1.2 (contd.-4)

COMPOUND (Ref.)	Structure	BOND LENGTH							BOND ANGLES				
		1	2	3	4	5	6	7	A	B	C	D	E
$RuCl(PPh_3)CO\{CH_2=(Me)N-C(H)NCH_2Me_2\}$[84]	c	2.049(10)	2.24 (10)	1.328(14)	1.300(14)	-	1.406(15)	1.498(14)	61.1 (4)	-	-	112.6(10)	"planar"
trans $RuH(PPh_3)CO$ (p-tolyl NC(H)N p-tolyl).[174]	1,b	2.183 (5)	2.248 (5)	1.308 (7)	1.315 (7)	-	-	-	59.8 (2)	94.3 (3)	91.2 (4)	114.7(5)	"planar"
$Os(\mu\text{-}H)(CO)_9\{NPh\text{-}C(Ph)NH\}$, I,II, two independent molecules in the asymmetric unit.[75]	k I.	2.198(23) Os(1)-N(1)	2.141(22) Os(3)-N(2)	1.417(34)	1.243(36)	-	-	-				121.7(25)	-
		2.193(23) Os(3)-N(1)											
	II.	2.132(19)	2.174(20)	1.464(32)	1.242(40)	-	-	-				115.3(20)	-
		2.188(20)											
$PPh_4[Cl_5Os\{NC(CCl_3)NCCl(CCl_3)\}].CH_2Cl_2$.[119]	as part of an ion	1.97 (1)	-	1.34 (1)	1.35 (1)	1.55 (1)	-	1.28 (1)	-	142.(18)	-	120.4(10)	-
$CoCl_4\{H_3CC(NH_2)_2\}_2$ (120)	salt	-	-	1.33	1.32	1.50	-	-	-	-	-	121.3	Central C atom slightly below plane
$Pd\{p\text{-tolyl NC}(CH_3)N\ p\text{-tolyl}\}_2$.[73]	b	2.038 (3)	2.038 (3)	1.322 (4)	1.322 (4)	1.512 (9)	1.412 (4)	1.412 (4)	63.5 (1)	94.0 (2)	94.0 (2)	108.4(3)	3.1
$Pd(\pi\text{-}C_5H_5(p\text{-}CH_3C_6H_9))N(H)((CH_3)Np\text{-tolyl})$. (73).	j	2.040 (6)	1.984 (7) $Pd\text{-}C_{aryl}$	1.285 (9)	1.350 (9)	1.492(11)	1.516(12)	1.518(15)	91.3 (3) N(1)-Pd-C_{aryl}	128.2 (5)	124.2 (6) Pd-C_{aryl}-C_{aryl}	122.0 (6)	5.2 Pd-N-C to C_{aryl}-C_{aryl}

TABLE 1.2 (contd.-5)

COMPOUND (Ref.)	BOND LENGTH								BOND ANGLES				
	Structure	1	2	3	4	5	6	7	A	B	C	D	E
$Pt(NH_3)_2\ CH_3((NH_2)-NH_2Cl_2H_2O$.[145]	salt	2.038	1.957	-	1.271	1.533	-	-	-	-	-	127.8	0.2
Pt(PhN-C(Ph)-NPh)$_2$.[67]	b	2.038(12)	2.022(12)	1.331(10)	1.340(10)	1.497 (1)	1.406(10)	1.401(12)	63.71	94.54	94.9	106.7	2.5
Pt{$C_6H_3(CH_2NMe)_2$} {p-tolyl-N(H)C(H)-N-p-tolyl)}.[65]	a	2.16 (1)	-	-	-	-	-	-	-	-	-	-	-
Pt{$C_6H_3(CH_2NMe)_2$} {p-tolyl NC(H)N-p-tolyl}.[65]	a	2.132 (6)	-	-	-	-	-	-	-	-	-	-	-
{2,6(Me_2NCH_2)$_2$} C_6H_3 Pt(μ-p-tolyl NC(H)Ni-Pr)HgBrCl.[70]	g	2.155 (9) Pt	2.16 (1) Hg	1.32 (1)	1.28 (2)	-	1.40 (1)	1.53 (2)	-	121.8(8)	123.5(8)	125.(1)	non-planar 0.15
Pt $(C_6H_5)_2N_3H_2\}_2$	i	1.99 (4)	1.90 (3)	at C1 1.41 (6)	at C2 1.34 (6)	1.47 (6)	-	-	87.9(1.4)	128.(3)	123.(3)	125.(4)	0.02
0.75 $C_6J_5CH_3$.(six-membered ring).[73]		1.93 (4)	1.96 (3)	1.24 (6) at C3	1.29 (6) at C4	1.57 (7)	-	-	84.5(1.4)	126.(3)	122.(3)	130.(4)	
				1.42 (5)	1.43 (6)	1.58 (7)						133.(5)	
				1.37 (6)	1.21 (6)	1.56 (6)						133.(4)	
Cu_2 PhNC(Ph)NPh$_4$[161]	g	2.019 (5)	2.026 (5)	1.328 (7)	1.334 (8)	1.547(7)	1.454(6)	1.434(6)	-	-	-	120.0(5)	"planar"

TABLE 1.2 (contd.-6)

COMPOUND (Ref.)	BOND LENGTH								BOND ANGLES				
	Structure	1	2	3	4	5	6	7	A	B	C	D	E
$HgC_6H_5\{CH_3C_6H_4\text{-}N\text{-}C(H)C_6H_4CH_3\}$ two independent molecules.[68]	a (I)	2.13 (3)	2.68 (2)	1.31 (4)	1.30 (4)	-	1.54 (5)	1.30 (1)	49	112	80	117	-
	c (II)	2.02 (3)	3.19 (2)	1.44 (4)	1.27 (4)	-	1.46 (4)	1.51 (4)	47	121	71	119	

NOTE: the structures of $CuCl_4\{H_3(C(NH_2)_2\}_2$,[120,158,159] and $Rh^{2.5}$ (N,N´di-p-tolylformamidine)$_3$ $(NO_3)_2$ have been established, but insufficient data was available for inclusion.[175]

TABLE 1.2 (contd.-7)

In the bridging, (Fig.1.3) case, the N-C-N angle does not depend on the substituents on the amidine and varies considerably - 115° - 124° with an average value of 117°. The large variation is possibly due to the wide compass of metal-metal interactions present in the complexes. As expected the N-C-N bridge angle is greater than the N-C-N chelate angle, and is similar to that found for bridging triazenes, 117°.[176]

Structural data for monodentate complexes is unfortunately sparse, and the N-C-N angle for Ph Hg [p-tolyl NC(H)N-p-tolyl], 117° can only tentatively be compared with that of the monodentate triazene complex N-N-N angle of 114°, which is found for *cis* [Pt(1,3-diphenyl triazene)$_2$(PPh$_3$)$_2$] C_6H_6.[176] What is clear is that the N-C-N angle for the monodentate formamidine complex is different (∿2°-3°), to that found for formamidine chelate 115°, and formamidine bridging ligands 120°-125°. The monodentate triazeno ligand complex has in comparison a significant difference in the value of its N-N-N angle (114°) compared to the average values for N-N-N chelate 103°, and N-N-N bridge 119° angles.

The C-N bonds in both the bidentate chelate (1.33Å, average), and the bridging (1.36Å, average) amidines are all of similar length. Their values indicate considerable multiple-bond character and lie between the average single and double bond covalent distances of 1.48Å and 1.24Å given by Schomaker and Stevenson,[177] for a range of organic molecules. They also agree well with the delocalised C-N (1.308Å) distance found in the benzamidinium cation.[77] The length of the bond appears to be virtually independent of

the amidine, the metal, and the bonding mode. The exception is bonding mode (C) (Fig.1.3) *e.g.* $TaCl_3\{C_6H_{11}NC(Me)-NC_6H_{11}\}\{C_6H_{11}NC(NHC_6H_{11})O\}$, where one C-N=1.57Å.

The C-C (5) distance between the amidine fragment and its central carbon atom substituent appears to be independent of the nature of the complex. The average C-C distance found (1.52Å), compares well with those found in salts of acetamidine 1.53Å (Cobalt), and 1.50Å (Pt salt),[120,145] and benzamidine (Re salt) 1.49Å,[77] and represents a normal $C(sp^2)$ - $C(sp^2)$ bond distance.

The M-N-C angle is greater in the bridging complexes (average = 119°) than the chelate (average = 95°) as we would expect. Formally, the nitrogen would be regarded as sp^2 hybridised, but the constraints of the ring force a reduction of 25° compared with the idealised angle of 120°. Ring strain will also be taken at the metal centre, where the size of the N-M-N angle is found to be dependent on the nature of the metal, *e.g.* Ta(V); average 60.4°,[68,169-172] Ru(II), 61.1°;[84] Pt(II), 63.7°;[67] Pd(II), 63.5°.[73] It is worth noting that the ionic radii of Pt(II) (0.52Å), and Pd(II) (0.50Å)[178] and hence their "ionic size" are very similar, as are their N-M-N anglesdespite different ligands being used. Therefore the size of the metal "ion" and hence its oxidation state may be an important factor in determining the size of the N-M-N angle.

The N-C(6,7)substituent distances, see Table 1.3, appear to be independent of the amidine and type of complex.

TABLE 1.3 The N-C distances for the nitrogen substituent groups

Group	Ref.	Average N-C	Bonding Mode of Ligand
C_6H_{11}	68	1.48	chelate
C_3H_7	170	1.46	chelate
CH_3	90	1.46	bridge
Ph	67	1.42	chelate
p-tolyl	73	1.41	chelate
Ph	69	1.44	bridge

The average N-C distance for all the complexes, 1.45Å is close to the pure single bond C-N value of 1.47Å.[79] and indicates that the delocalised NCN π-system is not extended significantly to the rings. This is also the conclusion reached from the ring torsion angles.

Considering the M-N bond lengths for the chelate (B), (Fig.1.3), σ, σ-bonded complexes, there appears to be two distinct groups. The $Pd\{PhNC(CH_3)NPh\}_2$ [73] and $Pt\{PhNC(Ph)NP_h\}_2$ complexes have an average bond length of 2.038Å, which compares well with $\{Pd(NH_3)_4\}$,[24] (M-N) = 2.044Å,[129] and $[Pd(en)]^{2+}$, (M-N)=2.030Å and 2.043Å,[180] for which metal to nitrogen π-bonding is absent. The other group consists of a number of molybdenum complexes,[98-99] and trans $RuH(PPh_3)_2$ CO{p-tolyl-NCH N p-tolyl},[174] for which the M-N bond lengths average 2.23Å. The latter bond lengths are similar to that found in $Mo(CO)_2C_5H_5$ (Ph-N-N-N-Ph), 2.15Å, which contains the related triazenido ligand.[176] A number of factors may explain the data. The palladium and platinum complexes are of a bis-

amidino type, and no other ligands are present on the metal. The other complexes have only one amidine group present and a number of other ligands which may substantially effect the M-N bond distance, *e.g.* there is a bond lengthening of the Ru-N(2) bond in the trans $RuH(PPh_3)CO$(p-tolyl NC(H)Np-tolyl) complex[174] because of the "trans-effect" of the hydride ligand opposite N(2). Thus, it appears that the presence of groups on the metal other than amidines have the effect of lengthening the M-N bond, and that "short" M-N amidine bonding is promoted by symmetric chelation.

Another possibility is that the molybdenum complexes are less delocalised than their palladium counterparts, and that there is a small amount of π-bonding occurring between the platinum/palladium and the nitrogen atoms. This seems unlikely since we have already noted the similarity of the bond lengths of complexes which contain no π-bonding, and the platinum and palladium amidine complexes.

Thirdly there is the matter of oxidation state, and hence ion size. Two complexes with the same formal oxidation states, and bonding modes, Pt(II) $\{PhNC(Ph)NPh\}_2$,[67] and Pd(II)$\{$p-tolyl NC(CH_3)N-p-tolyl$\}_2$[73] have similar M-N bond lengths - (2.038Å and 2.022Å), and (2.038Å and 2.038Å) respectively. Since the ligands and the metals differ, it is clear that oxidation state and hence ion size has an effect on the M-N distance.

In bridging amidines the M-N distances average 2.10Å which is similar to that found for the average M-N bond in bridging triazenes 2.02Å.[176] The variation in values is

high and they appear to be independent of the amidine and the other ligands present. Worthy of note are the complexes $Cu_2[PhNC(Ph)NPh]_4$;[161] (2.02Å), $Re_2\{PhNC(CH_3)NPh\}_2Cl_4$;[112] (2.08Å), and $Cr_2\{CH_3NC(Ph)NCH_3\}_4$;[90] (2.03Å) which all have very short M-N distances, as well as strong metal-metal interactions.

The general amidine bonding modes have been considered above. However, there are a number of less well known modes which can be compared with those already discussed.

The insertion products formed when benzonitrile or methylene are inserted into the chelate ring gives rise to bonding mode (i) (Fig.1.3). Corresponding changes in the structural parameters occur. The symmetrical PtN_4 structure formed in the Pt $HNC(C_6H_5)NC(C_6H_5)NH_2$ complex involves a six-membered ring with extensive delocalisation. As a result the mean Pt-N distance (1.96Å) is similar to that found for chelate platinum and palladium bis-amidino complexes, but compares more closely to the Pt-N distance in trans $\{Pt(NH_3)_2(N\text{-methylimidazole})_2\}Cl_2 2H_2O$;[181] Pt-N 2.01Å. These values are slightly lower than those normally found for platinum (II) complexes (2.05Å),[182] and indicate some multiple bond character. The C-N bond lengths (average=1.34Å), definitely show considerable π-character. They are similar to those found in s-triazene (1.319Å)[183] which is itself extensively delocalised. The average of the N-C-N angles is $Pt\{HN(Ph)NC(Ph)NH\}_2$ (127°) indicates an opening up of the angle compared to bridging and chelate N-C-N angles, because of the six-membered ring formation.

In the tungsten-methylene case $[W_2(\mu\text{-}CO)_2\{\mu\text{-}HC(N\text{-}3,5\text{-}xylyl)_2\}_2\{HC(N\text{-}3,5\text{-}xylyl)_2\}\{N\text{-}3,5\text{-}xylyl)CH(N\text{-}3,5\text{-}xylyl)CH_2\}$,[72] only one CH_2 group is inserted and the resultant ring is asymmetric. As a result the M-N distance is larger and the N-C-N angle increased.

The *ortho*-metallation-bonding mode (j) (Fig.1.3), also influences the bonding parameters. The π-cyclo-pentadienyl, N,N´-di-para-tolyl-acetamidino-palladium structure[73] has a novel six-membered ring. The Pd-N distance (2.040Å) is similar to that found for the σ, σ, bidentate platinum and palladium *bis*-amidino complexes. This indicates there is little π-interaction between the ring and the palladium. The Pd-C distance (1.984Å) can be compared with 1.98Å found in μ- diphenylacetylene-*bis*(μ-pentaphenylcyclopentadienyl)di-palladium(I).[183] The relevant M-N-C and N-C-N angles in the complex are as expected, greater than those found for the chelate complexes.

The mixed metal complex $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Pt(\mu\text{-}\{p.tolyl\ NCHNPR^i\})\ Hg\ Br\ Cl]$[70] has an unusual feature in that the M-N distances are very similar PtN(1) = 2.155Å, HgN(2) = 2.156Å, which contrasts with the differing metal-nitrogen bond lengths found in [(cycloocta-1,5-diene)(p-tol-NNNEt)$_2$IrHgCl],[184] Ir-N(1) = 2.10Å, Hg=-N(3) = 2.42Å which contains related triazenido ligand. Also of note is the lack of planarity of the five-membered ring, which may be due to steric effects or the length of the metal-metal bond contained in the ring.

It is clear that a wide variety of amidine bonding modes have now been characterised by X-ray crystallography;

however, before more than qualitative comparisons can be undertaken a lot more structural data is required.

1.6 Industrial Uses of Metal-Amidines

The following section is not meant to be an exhaustive survey of industrial patents involving amidine-transition-metal compounds, but is an illustration of some of the industrial uses of amidine-transition-metal interactions.

Daugherty and Vaugh for instance,[185] used formamidine disulphide hydrochloride to prevent multi-step room temperature etching of copper or copper alloy printing plates, by unsaturated $FeCl_3$ solution (16.5-31.5%). The amidine protective coating could be removed from parts of the plates by brushing, allowing one-step etching by the $FeCl_3$ solution without the problem of lateral undercutting.

L.A. Lundberg[186] used a mixed Cu-benzamidine HCl promoter to improve gel times by a factor of 2-3 for elastomer-vinyl-aromatic compositions, (butadiene/styrene/divinylbenzene).

Diarylformamidines,[187] have also been used as promoters in oxidative poly-(phenylene ether) formation. High molecular weight poly-(phenylene ethers) were prepared by self-condensation of phenols, *e.g.* 2,6-xylenol, in the presence of amine-copper complexes, *e.g.* (Bu_2NH-$CuBr_2$, and N, N´-diphenyl-formamidine. Products, *e.g.* poly-2,6-dimethylphenylene oxide (93% yield) formed using the formamidine had an improved intrinsic viscosity.

Finally, Bayer A.G.,[188] investigated the effect of soluble mercury(II), zinc(II), copper(II) and iron(II) compounds and amidines as catalysts for isocyanate polyaddition reactions. A number of the mixtures were reported to have good catalytic activity.

The review presented highlights the large areas of the transition-metal chemistry of amidines still to be explored. Interest arises from the synthetic chemistry, the variety of bonding modes and structural aspects in general, and from reactions of the complexes. Furthermore the work has an industrial dimension as outlined in the introduction to the survey, which has not been widely explored. This thesis is concerned with extending this work by the synthesis, using a variety of routes, and characterisation of amidine complexes of platinum palladium and nickel.

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CHAPTER TWO

ASPECTS OF THE MASS SPECTRAL FRAGMENTATION PATTERNS OF AMIDINES

Simple amidines have been used extensively as ligands in transition metal chemistry,[1] and many of these studies have reported mass spectral fragmentation patterns.[1] Mass spectroscopic studies on the free ligands have, however, been limited. Previous studies have involved the fragmentation patterns of N,N´dimethyl-N-phenylformamidine,[2-7] and tetrafluoroformamidine (CN_2F_4).[8] For simple amidines, however, only the detailed study of Keats[9] on N,N´diphenylformamidine and N,N´di(chlorophenyl)formamidines, and a less detailed study of N,N´diphenyl- and N,N´dicyclohexylformamidines by Saeed[10] exist.

As part of an investigation of the properties of simple amidines, the mass spectra of a number of these have been recorded. Three examples (1) N,N´diphenylformamidine, (2) N,N´diphenylacetamidine, and (3) N,N´diphenylbenzamidine have been studied in detail, using accurate mass measurements. The patterns of the other amidines will be discussed more generally with reference to the detailed fragmentation patterns mentioned above.

Spectral details are recorded in Tables 2.1, 2.2 and 2.3 and (Figs. 1.1 - 1.3).

The results for N,N´diphenylformamidine {PhNCHN(H)Ph} are in agreement with those found previously.[9,10] They indicate a CH-NH bond rupture to produce two fragments $C_7H_6N^+$ (m/e104), and $C_6H_6N^+$ (m/e92). Hydrogen migration also takes place to produce a stable aniline type ion $C_6H_7N^+$ (m/e93) which is the base peak of the spectrum. The phenylisocyanide ion $C_6H_5NC^+$ (m/e103),

TABLE 2.1 Empirical formula of fragment ions in the mass spectrum of N,N'-diphenylformamidine

m/e	Formula	Relative Intensity %
196	$C_6H_5NCHNHC_6H_5$	63
195	$C_6H_5NCHNC_6H_5$	24
121		11
104	C_6H_5NCH	24
93	$C_6H_5NH_2$	100
92	C_6H_5NH	4
77	C_6H_5	58
76	C_6H_4	3
71		2
69		2
66	C_5H_6	14
65	C_5H_5	10
57		5
55		5
51	C_4H_3	17
44		13
41	CN_2H	8
39	C_3H_3	8
38	C_3H_2	3

TABLE 2.2 Empirical formula of fragment ions in the mass spectra of N,N′ diphenylacetamidine

m/e	Formula	Relative Intensity %
210	$C_6H_5NC(CH_3)NHC_6H_5$	27
209	$C_6H_5NC(CH_3)NC_6H_5$	19
180		2
167		2
118	$C_6H_5NCCH_3$	100
117	$C_6H_5NCCH_2$	8
104	C_6H_5NCH	2
93	$C_6H_5NH_2$	11
92	C_6H_6N	1
91	C_6H_5N	2
77	C_6H_5	81
76	C_6H_4	2
75		1
66	C_5H_6	2
65	C_5H_5	4
64	C_5H_4	1
51	C_4H_3	20
50	C_4H_2	1
42	CN_2H_2	2
41	CN_2H	2
40	C_3H_3	1
39	C_3H_2	4

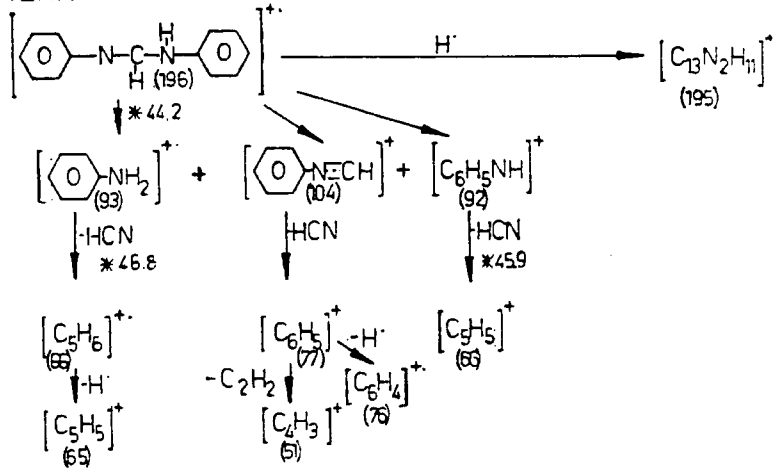
TABLE 2.3 Empirical formula of fragment ions in the mass spectrum of N,N´ diphenylbenzamidine

m/e	Formula	Relative Intensity %
272	$C_6H_5NC(C_6H_5)NHC_6H_5$	10
271	$C_6H_5NC(C_6H_5)NC_6H_5$	5
182		1
180	$C_6H_5NCC_6H_5$	100
167		1
104	C_6H_5NCH	1
77	C_6H_5	37
76	C_6H_4	1
65	C_5H_3	1
51	C_4H_3	9

which had been reported previously,[9] was not found in these studies. Further fragmentation by loss of HCN occurred to give various $C_nH_n^+$ species.

For both N,N´ diphenylacetamidine and N,N´ diphenylbenzamidine the stable substituted aniline ions (PhN-HR´), (R´=Ph,CH_3) similar to the one described above are not formed. Instead the base peak of the spectra corresponds to a stable $[RNCR]^+$ ion R´=R=Ph, (m/e 180), R=Ph, R´=CH_3 (m/e 118). This may be due to delocalisation factors, or the difficulty of hydrogen migration in these compounds. The aniline $C_6H_7N^+$ (m/e 93) ion is formed in the case of N,N´ diphenylacetamidine, but it is a minor part of the fragmentation pattern. The $[RNCR´]^+$ ion undergoes further simple fragmentation to give the $[C_6H_5]^+$ (m/e 77) ion.

FIGURE 1 N,N' DIPHENYLFORMAMIDINE FRAGMENTATION PATTERN



FIGURES 2.1 - 3.

FIGURE 2 N,N' DIPHENYLACETAMIDINE FRAGMENTATION PATTERN

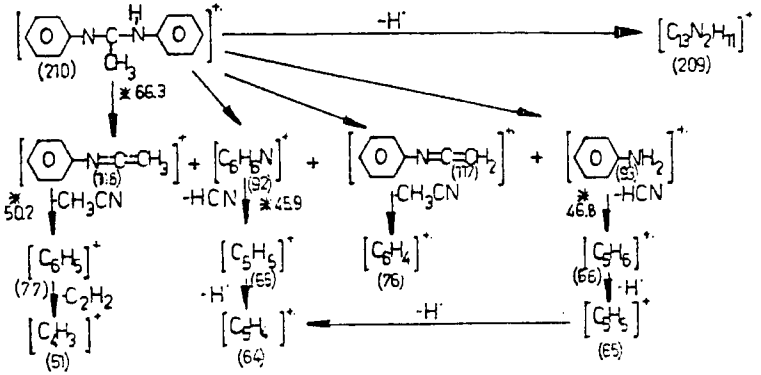
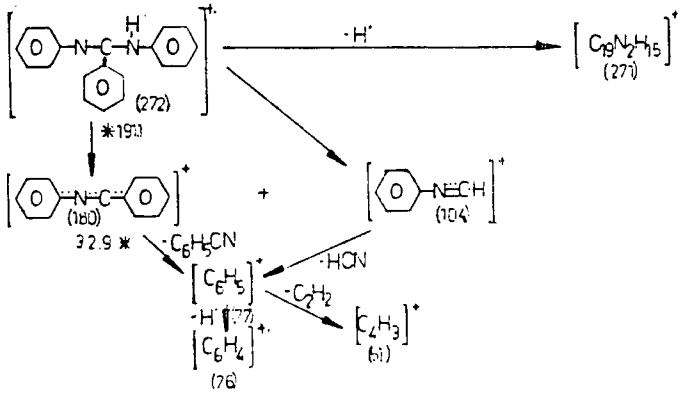


FIGURE 3 N,N' DIPHENYLBENZAMIDINE FRAGMENTATION PATTERN



In all three cases a strong molecular ion was noted and an $[M-1]^+$ peak due to the loss of H· from the parent.

Metastable ions were found to support the important transitions in the fragmentation patterns of the three molecules. The patterns are described in Figures 2.1, 2.2 and 2.3, and since the exact structure of the fragments formed under electron impact is not known, the structures and mechanisms presented are only to indicate the origin of fragments. A strong metastable ion was found in the spectrum of N,N´-diphenylformamidine at m/e 44.2 corresponding to the transition m/e 196→93 and confirming the loss of the PhNC fragment. For N,N´ diphenylacetamidine the metastable at m/e 66.3 supports the important m/e 210→118 transition corresponding to loss of PhNH, and for N,N´ diphenylbenzamidine a metastable at m/e 191.1 (m/e 272→180), corresponds to the loss of the same group.

The key in Table 2.4 will be used in the discussion of the more general findings of this study.

All the amidines studied showed a parent molecular ion M; I m/e 44(4%), II m/e -, III 196(68%), IV 224 (48%), V 224 (19%); VI 58 (62%); VII 210 (27%); VIII 238 (51%); IX 238 (13%); X 238 (38%); XI 246 (9%); XII 100 (4%); XIII 120 (67%); XIV 148 (25%); XV 272 (10%); XVI 300 (19%); XVII 308 (18%); XVIII 356 (85%), and an $[M-1]^+$ peak due to the loss of H· from the parent. The exception is chloroformamidine (II), where the parent ion was not found due to C-Cl bond cleavage under electron impact.

All the substituted phenyl formamidines studied show a substituted aniline type of ion as their base peak. Slight

TABLE 2.4

I: Formamidine HCl; $HCN_2H_3.HCl$.

II: Chloroformamidine HCl; $ClCN_2H_3.HCl$.

III: N,N´ diphenylformamidine; $PhNC(H)N(H)Ph$.

IV: N,N´di-para-tolylformamidine; $p\cdot CH_3\cdot C_6H_4\cdot NC(H)N(H)\cdot C_6H_4\cdot CH_3\cdot p$.

V: N,N di-ortho-tolylformamidine; $o\cdot CH_3C_6H_4\text{-}NC(H)N(H)\cdot C_6H_4CH_3\cdot o$.

VI: Acetamidine HCl; $CH_3CN_2H_3HCl$.

VII: N,N´diphenylacetamidine; $PhNC(CH_3)N(H)Ph$.

VIII: N,N´di-para-tolylacetamidine HCl; $p\cdot CH_3C_6H_4NC(CH_3)N(H)C_6H_4CH_3\cdot p.$ HCl

IX: N,N´di-ortho-tolylacetamidine HCl; $o\cdot CH_3C_6H_4NC(CH_3)N(H)C_6H_4CH_3\cdot o.$ HCl.

X: N,N´dibenzylacetamidine HCl; $PhCH_2NC(CH_3)N(H)CH_2Ph.HCl$.

XI: N,N´di-para-fluorophenylacetamidine; $p.F\cdot C_6H_4NC(CH_3)N(H)\cdot C_6H_4\cdot F\ p.$

XII: T-butylamidine HCl; $C_4H_9CN_2H_3.HCl$.

XIII: Benzamidine HCL; $C_6H_5CN_2H_3.HCl$.

XIV: N,N´dimethylbenzamidine; $CH_3\cdot NC(Ph)N(H)CH_3$.

XV: N,N´diphenylbenzamidine; $PhNC(Ph)N(H)Ph$.

XVI: N,N´di-para-tolylbenzamidine; $p.CH_3\cdot C_6H_4\cdot NC(Ph)N(H)\cdot C_6H_4CH_3.p.$

XVII: N,N´di-para-fluorophenylbenzamidine; $p.F\cdot C_6H_4NC(Ph)N(H)C_6H_4\cdot F\cdot p.$

XVIII: N,N´di-para-isopropylphenylbenzamidine; $p.CH_3CH_3CH_2\cdot NC(Ph)N)H)C_6H_4CH_2CH_2CH_3\cdot p.$

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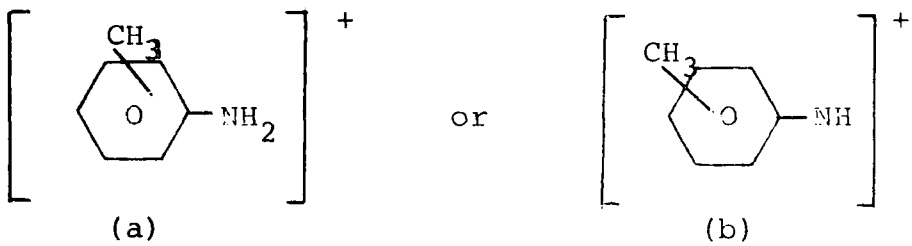
differences between the *ortho* (V) and *para* (IV) tolyl derivatives were noted, though strong peaks observed for both ions (a) and (b).



(a) (b)

In the *ortho* case, the (a) type ion is slightly more prominent (m/e 107), and in the *para* case the (b) type (m/e 106) is stronger. These differences may be attributed to small differences in resonance. Intense peaks are also found for the $[CH_3C_6H_4]^+$ ion (m/e 91) in both these cases.

The acetamidines and benzamidines in general have the substituted $[RCNR']^+$ ion as their base peak, the exceptions being N,N dibenzylacetamidine (X) where the occurrence of H migration produces a base peak due to the $[C_6H_5\text{-}CH_2\text{-}NH]^+$ (m/e 106) ion, and N,N´dimethylbenzamidine (XV) where the $[M\text{-}1]^+$ peak is the base peak. A very strong $[RCNR']^+$ ion was also found in the N,N´dimethylbenzamidine spectrum. Strong peaks due to the $[C_6H_5]^+$ ion (m/e 77) were found in all cases, and for N,N´di-p-fluorophenylacetamidine (XI) and N,N´di-p-fluorophenylbenzamidine (XVII) strong peaks at m/e 95 attributable to the $[C_6H_4F]^+$ ion were found.

The spectrum of N,N´di-*p*-isopropyl-phenylbenzamidine (XVIII) shows some side chain fragmentation in the initial breakdown stage. The propyl group loses a methyl group and two hydrogen groups, whilst a concomitant total side chain loss occurs:

the latter being the more favoured process.

The unsubstituted amidines formamidine (I), chloroformamidine (II), acetamidine (VI), tert-butylamidine (XII), and benzamidine (XIII), all undergo a similar breakdown pattern which involves cleavage of the bond between the substituent and the central carbon atom of the amidine moiety. Thus the ion $[CN_2H_3]^+$ (m/e 43) is produced in all cases. Supporting peaks for (XII) at m/e 67 $[C_4H_9]^+$ for XIII at m/e 77 $[C_6H_5]^+$ were also found. Supporting peaks for the other unsubstituted amidines were not found because peaks below m/e 35 were not recorded. For both (XII) and (XIII) other fragmentation routes were observed.

(1) $[C_6H_5CN_2H_3]^+$ (m/e 120) $\xrightarrow[(16)]{-(NH_2)}$ $[C_6H_5CNH_2]$ (m/e 104) (base peak.

(2) $[C_6H_5]^+$ (m/e 77) $\xrightarrow[(26)]{-CH\ CH}$ $[C_4H_3]^+$ (m/e 51).

(3) $[C_4H_9CN_2H_3]^+$ (m/e 100) $\xrightarrow[(15)]{-CH_3}$ $[C_3H_6CN_2H_3]$ (m/e 85)

(4) $[C_4H_9]^+$ (m/e 57) $\xrightarrow[(15)]{-CH_3}$ $[C_3H_6]^+$ (m/e 42)

In conclusion the spectra of substituted acetamidines and benzamidines are similar in that their fragmentation involves an $[RNCR']^+$ ion, possibly stabilised by resonance. The substituted formamidines however, fragment *via* a substituted aniline type of ion $[R'-C_6H_7N]^+$, which may be due to hydrogen migration which is difficult in the former cases.

The important fragmentation for unsubstituted amidines was found to be that involving cleavage of the substituent to central carbon atom of the amidine moiety bond.

Experimental:

The mass spectra were determined on pure samples using an A.E.I. MS-9 mass spectrometer and a V.G.7070E mass spectrometer. The samples were analysed by a direct insertion probe at an ionising current of 70 eV. The ion source temperature was 190^{o}C. Elemental compositions were determined by accurate mass measurement.

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CHAPTER THREE

A SPECTROSCOPIC STUDY OF A LITHIOAMIDINE TOGETHER WITH A ^{13}C N.M.R. STUDY OF A SERIES OF AMIDINES

INTRODUCTION

Considering the widespread use of lithium-amidine reagents in transition - metal and main-group chemistry[1], they have been little studied[2] and their molecular form in solution is not known. An example compound, N,N'di-*p*-fluorophenyl-benzamidinolithium, has been prepared and studied by mass spectroscopy, infra-red and n.m.r. techniques.

3.1 Experimental

Three aliquots (3.08g., 10mmol) of DPFPBAH were placed in flasks which had previously been flame dried and purged vigorously with nitrogen. The amidine in each flask was dissolved by one of three solvents; hexane (100ml.), tetrahydrofuran (100ml.), or monoglyme (100ml.). Each solution was then cooled to $0^{o}C$ using an ice-bath, and 10mmol of n-butyl lithium (1.54M) added to each flask. The solutions were allowed to warm to room temperature, and stirred for a further 30 minutes to allow the reaction to fully develop. All of the solutions were yellow-green in colour at this stage. The solvent was removed in each case *in vacuo* and a viscid yellow material resulted in all cases. The infra-red and mass spectra of the T.H.F. derived solid were taken at this stage. The solids were extracted with d^{6}-benzene, and the solutions sealed in n.m.r. tubes which had been baked at $150^{o}C$ for several days. The solutions were used to yield a series of ^{1}H, ^{13}C and ^{19}F n.m.r. spectra.

3.2 Infra-red

(nujol mull CsI plates), 1600w., 1260s., 1210w., 1100 v.s., 1020 v.s., 870w., 875m.sh., 805v.s., 730w., 705v.w., 600w., 520w.br., 470m., 455m., 390m., 250m., cm^{-1}.

3.3 Mass Spectroscopy

Because of the sensitive nature of the compound (air, moisture), analysis was carried out by chemical ionisation using isobutane as carrier.

TABLE 3.1 The mass spectrum of N,N´di-*p*-fluorophenyl-benzamidino lithium.

m/e	assignment	% intensity
463	$^{7}LiC_{19}N_2F_2H_{13}(T.H.F.)C_6H_5$	1
368	$^{7}LiC_{19}N_2F_2H_{13}\{C_4H_6\}$	1
354	$^{7}LiC_{19}N_2F_2H_{13}\{C_3H_4\}$	14
313	$^{7}LiC_{19}N_2F_2H_{12}$	46
312	$^{7}LiC_{19}N_2F_2H_{11}$	96
311	$^{7}LiC_{19}N_2F_2H_{10}$	43
242	$F\text{-}C_6H_4N\text{-}C\text{-}Ph\{C_3H_7\}$	15
199	$F\text{-}C_6H_4N\text{-}C\text{-}Ph\{H\}$	96
105	$PhCN\{2H\}$	18
72	C_4H_8O	100

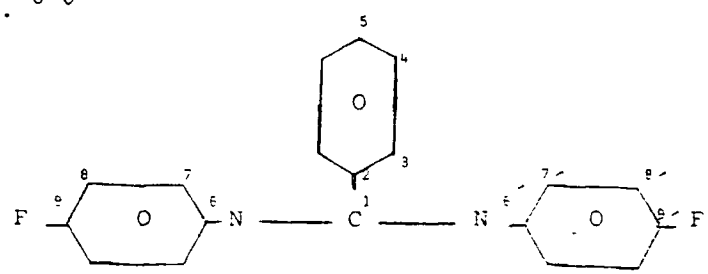
3.4 N.M.R.

(See Tables 3.2, 3.3 and 3.4 and Figure 3.1).

TABLE 3.2 ^{13}C N.M.R. of lithium N,N´di-fluoro-phenylbenzamidine solvates and N,N´di-fluoro-phenylbenzamidine

COMPLEX	C_1	C_2	C_3	C_4	C_5	C_6/C_6'	C_7/C_7'	C_8/C_8'	C_9/C_9'	SOLVATE
Li(DPFPBA) THF	153.95	133.95	128.04	127.38	129.07	140.71	121.39 br.	114.01 (J_{C-F}=22)	157.56 (J_{C-F}=240)	66.34(CH_2-O), 24.38(CH_2)
Li(DPFBA) MONO-GLYME	153.60	134.10	127.18	127.40	127.98	140.57	121.36 br.	114.03 (J_{C-F}=22)	157.55 (J_{C-F}=240)	70.85(CH_2-O), 57.29(CH_3-O)
Li(DPFBA) HEXANE	153.18	133.99	127.19	127.31	129.17	140.50	121.33 br.	114.03 (J_{C-F}=21)	157.54 (J_{C-F}=241)	33.81(CH_2-{CH_2}, 28.90 (i), 17.82(CH_2{CH_2-CH_3}) 12.62(CH_2{CH_3})
DPFBAH	154.57	135.27	128.51	128.81	-	139.63	122.73 br.	115.40 (J_{C-F}=22)	158.96 (J_{C-F}=241)	

KEY: All shifts relative to T.M.S.=0 Hexane contains n-hexane and isomers hence the extra peak.
All spectra run in C_6D_6. Carbons referenced from Figure 3.1 - denotes not observed.
All J values in Hz.



(Figure 3.1)

TABLE 3.3 ^{1}H N.M.R. of Li(DPFPBA) Solvates (δ values)

H *ortho* F-ring	H *meta* F-ring	H's C-ring	Ratio of Li(Am) to Solvate	Solvate
7.01d{4H} (J=8)	6.95d{4H} (J=7)	6.85s{5H} 6.82s 6.79s (J=8)	1Li(AM):1Hexane (Solvate:0.88m {CH_3},1.38m. {CH_2}, 3.38br. {CH_2}	Hexane
7.02d{4H} (J=8)	6.96d{4H}	6.85{5H} 6.26 6.79 (J=8)	1Li(AM): 0.5 T.H.F. (Solvate: 3.59br. {4H} 1.47br. {4H}	T.H.F.
7.03d{4H} (J=8)	6.96d{4H} (J=8)	6.82 6.83 6.86 (J=8)	1Li(Am): 2 Mono-glymes (Solvate: 3.90s{4H} 3.18s. {6H}.	Monoglyme

KEY: all shifts relative to T.M.S. = 0 in p.p.m., s = singlet, d = doublet, m = multiplet. J values given in Hz.

TABLE 3.4 ^{19}F N.M.R. of Li(DPFBA) Solvates

Complex Solvate	^{19}F Signal p.p.m.
Li(DPFBA) T.H.F.	-120.05
Li(DPFBA) Hexane	-119.94
Li(DPFBA) Mono-glyme	-120.05
DPFPBA	-122.37 †

† External $CFCl_3$ was used as reference for the complexes, and internal $CFCl_3$ for DPFPBA.

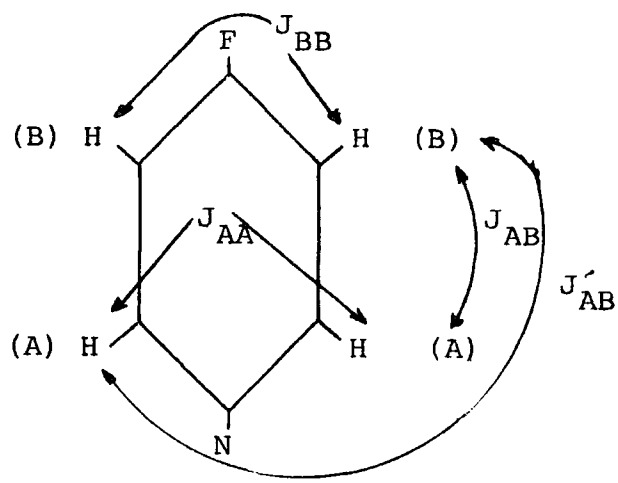
3.5 Discussion

The infra-red data has two notable features, the first as expected is the absence of an N-H str. vibration indicating that lithiation has taken place. Secondly bands at 1600 cm^{-1} and 1210 cm^{-1} by their position and intensity indicate a symmetrical bidentate bonding mode similar to that found for $Pd\{p\text{-}CH_3\text{-}C_6H_4NC(H)NC_6H_4\text{-}CH_3\text{-}p\}_2$,[3] which has delocalised N-C-N skeletons present. It is not possible to differentiate between chelate or bridging modes of bonding.

The reactive nature of the lithio-amidine and the use of an alkane carrier gas in the C.I. mass spectrum caused a number of interactions. The carrier gas contributions to the peaks are enclosed in brackets in Table 3.1. The ion Li(DPFPBA), (m/e 314), was not seen but the fragments around this species indicate fragments of an oligomer, or loss of protons in the spectrometer. The higher masses found cannot be assigned with any degree of certainty; however their presense is consistent with the oligomeric nature expected of a lithio-amidine complex, and which has been reported for related lithium nitrogen systems.[4] T.H.F. (m/e 72) is noticeably present.

The single ^{19}F signal noted for all the complexes is in agreement with symmetrical bonding, and rules out metallation of one of the rings or monodentate bonding, since these would require two ^{19}F signals instead of the one found experimentally. Interestingly Knoth[5] found a similar result for the analogous di-*p*-fluorophenyltriazene-lithium complex with one ^{19}F n.m.r. signal being noted at -123.99 p.p.m. in T.H.F. The small shifts upfield *ca.* 2 p.p.m. in the ^{19}F n.m.r. spectra are possibly due to greater shielding of the fluorines because of bond polarisation in the amidino ligand. A similar upfield shift for the C_1 and C_9 carbons (Figure 3.1), is present in the ^{13}C spectra, and occurs for the same reason. The n.m.r. spectra of the amidine and the lithio complexes are very similar with slight upfield shifts being noted for the carbons of the lithio derivatives. The J_{C-F} coupling constants found for the C_8 and C_9, (Figure 3.9) carbons of the amidine and its lithio derivatives were found to be similar to those found for fluoro-

benzene, of 245 and 21Hz.[6] The signal for C_6/C_6^1 (Figure 3.1) was very weak and considerably broadened. There was no evidence of asymmetry or metallation of the rings, again this is evidence for symmetrical bonding. The proton n.m.r. shows two distinct ring systems, again as expected for symmetric bonding. The "quartet" found in the aromatic region δ7.02-6.95 is "fingerprint" evidence that these signals are due to the *para* di-substituted fluorine containing rings. Quantum mechanical considerations predict no less than ten lines for each nucleus A and B (Figure 3.2). However, practically a "quartet" of signals as found in our



(Fig.3.2)

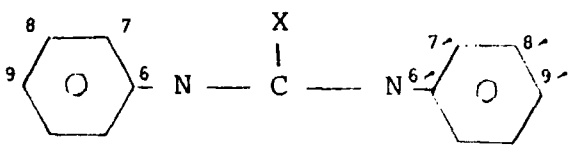
spectra is observed. The observed coupling constant 7-8Hz are not J_{AX} but either a good approximation to it or a J_{H-F} coupling constant; it is not possible to differentiate between these coupling constants. In both the ^{13}C and ^{1}H n.m.r. spectra there is evidence for the presence of solvate. Using the integration values from the proton spectra, an approximation of the amount of solvate present was calculated. Because of the errors involved the figures should only be regarded as approximate. The data indicated the following formulations, Li(Am)Hexane; Li(Am)0.5 T.H.F., Li(Am).2.Monoglyme.

The data found is consistent with an Li(Am) (Solvent) species being formed which have symmetrically bonded, bidentate amidine groups present.

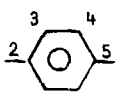
The complexes are analogous to those described recently by Snaith[7] as $Li^+[RN \cdots C(R') \cdots NR]^-$, and are related more to the η^3-aza-allyl type of complex $Li^+[CH_2 \cdots CR \cdots NR]^-$,[8] than to the "ionic" allyl bonded LiC_3H_5[9] type of complex.

3.6 ^{13}C n.m.r. of Parent Amidines

The data is presented in Table 3.5. The numbering system corresponds to Figure 3.3.



(Fig. 3.3)

when X-Ph,  X may also be H, CH_3, t-butyl or Cl. $C_9/C_{9'}$ may be a CH_3 group or a proton.

The compounds should be regarded in two groups.

TABLE 3.5 ^{13}C N.M.R. DATA FOR PARENT AMIDINES

AMIDINE	C_1	C_2	C_3	C_4	C_5	C_6/C_6^1	C_7/C_7^1	C_8/C_8^1	C_9/C_9^1	CH_3	CH_2	CH	t-but C		SOLVENT
Formamidine HCl	161.34														d^6D.M.S.O.
Chloroformamidine HCl	166.65*														d^6D.M.S.O.
Acetamidine HCl	172.14									22.13					d^6D.M.S.O.
t-Butyl Amidine HCl	176.95									27.31			36.31		$CDCl_3$
Benzamidine HCl	166.21	135.80	128.60	125.50	130.17										$CDCl_3$
N,N'Dimethylbenzamidine	159.89	135.33	127.65	127.26	128.31					32.14					$CDCl_3$
N,N'Diphenylformamidine	149.92					145.24	119.11	129.64	123.30						$CDCl_3$
N,N'Diphenylacetamidine	152.52					144.49	120.54	128.34	122.62	17.86					$CDCl_3$
N,N'Dibenzylacetamidine HCl	158.88					142.38	124.85	129.88	127.32	16.34	49.96				$CDCl_3$
N,N'Di-P-Fluorophenylacetamidine	153.07					141.90	122.35	115.42 (J_{C-F}=22)	156.68 (J_{C-F}=239)						C_6D_6
N,N'Diphenylbenzamidine	154.49	131.72	128.34	129.51	125.74	143.46	121.06	128.73	122.49						$CDCl_3$
N,N'Di-P-Tolylbenzamidine	154.21	135.10	127.93	128.47	124.05	142.70	121.45	128.99	131.98	20.46					$CDCl_3$
N,N'Di-P-Fluorophenylbenzamidine	154.20	134.18	127.71	128.40	-	139.60	121.88	114.56 (J_{C-F}=20)	158.01 (J_{C-F}=239)						$CDCl_3$
N,N'Di-P-Isopropylphenylbenzamidine	154.21	135.75	128.08	128.70	129.25	142.51	121.06	126.32	143.91						$CDCl_3$

KEY: All shifts (ppm) relative to T.M.S. = 0, - indicates peak not seen, * decomposition of sample was occurring in D.M.S.O., signal due to formamidine noted.

The first group consists of the hydrochlorides, the spectra of which should be regarded as amidinium cation spectra, which have been shown to absorb at slightly lower fields than the free amidines.[10] Taking the series as a whole, there appears to be little correlation between the nature of the substituent on the C_1 carbon (Figure 3.3), and the chemical shifts observed, A few simple observations were noted. The electron-withdrawing Cl group causes a shift (5 p.p.m.) of the N-C-N, C_1,signal (Figure 3.3), in chloroformamidine HCl (166.6 p.p.m.) downfield of that of the C_1 signal of formamidine HCL (161.3 p.p.m.). The increased crowding effects of the methyl group in acetamidine HCl, and the t-butyl group in t-butylamidine HCl cause a similar shift downfield of the C_1 signal of formamidine HCl. The second series consists of the free N,N´disubstituted amidines, and a slight upfield shift is noticeable for the C_1 (Figure 3.3) signal in the sequence Ph>CH_3>H. The difference between the acetamidine and benzamidine C_1 signals is small. In general, where data for comparison is available, the C_1 (Figure 3.3) carbon of amidines resonates at a higher field than in the corresponding amides (*e.g.* $HCONH_2$[1]; C_1-167.6 p.p.m.) or carboxylic acids (*e.g.* HCOOH[1]; C_1-166.3 p.p.m.); CH_3COOH[2][1]; C_1-177.2 p.p.m.; C_2-21.1). Other atoms such as the C_2 carbon (Figure 3.3), show a similar effect in the same direction.

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CHAPTER FOUR

AMIDINO - COMPLEXES OF d^8 IONS OF THE NICKEL GROUP ELEMENTS; CARBOXYLATO ANALOGUES

INTRODUCTION:

This chapter is concerned with the synthesis, and study of metal-amidine complexes to provide background information on metal-nitrogen bonded systems, relevant to understanding the catalytic processes involving organonitrogen compounds. In catalysis the platinum group metals are widely used as both the metal and in complex form. Amidine complexes are important in this context, and this chapter describes the preparation and characterisation of a number of bis-amidino nickel, palladium and platinum (II) complexes. Their synthesis was achieved by the reaction of the metal (II) chloride or metal bis-benzonitrile dichlororide with lithio-amidines, *viz*,

$$MCl_2 \text{ or } M(PhCN)_2Cl_2 + \text{Li amidine} \longrightarrow [M(\text{amidino})_2]_n + 2LiCl \qquad n = 1,2$$

4.1 Notation

In this thesis a shorthand notation for amidines has been employed for the chapters dealing with transition metal amidine complexes, *i.e.* DPTBAH = N,N´-di-(p-tolyl)benzamidine. The H suffix denotes that the amidine is the parent amidine with a N-H group. If the final H is omitted the shorthand refers to the amidino group, *i.e.* DPTBA = N,N´-di-(*p*-tolyl)-benzamidino group = [p-tolylN^{----} C(Ph) $^{----}$ Np-tolyl].

4.2 Experimental

The first steps in the synthesis of carboxylate analogues, involve lithiation of an amidine, and its subsequent reaction with a metal compound. The procedure is similar in all cases, hence the method will be described in detail only for the preparation of Pt{*p*-$FC_6H_4NC(C_6H_5)NC_6H_4F$-*p*}$_2$. Where necessary further details and variations in work up procedure will be noted for each complex prepared.

All experimental manipulations were carried out under dry nitrogen, reactants being added against a counter-current of nitrogen gas.

4.2.1 Reaction of $Pt(PhCN)_2Cl_2$ with [*p*-$FC_6H_4N(Li)C(C_6H_5)NC_6H_4F$-*p*]

DPFBAH, (1.5400g, 5mmol) was dissolved in diethyl ether (50ml.) producing a light yellow solution. The solution was cooled by means of an icebath, and an equivalent molar amount of n-butyl-lithium (1M in hexane) added *via* a syringe.

The solution was then allowed to reach room temperature whilst being stirred. On reaching room remperature the solution was yellow-green in colour; stirring at room temperature was undertaken for 30 minutes to allow for complete reaction. The solution was then frozen to -196°C by immersion in liquid nitrogen, and solid platinum bis-benzonitrile dichloride ($Pt(PhCN)_2Cl_2$; 1.180g. 2.5mmols) added. The solution was then allowed to reach room temperature whilst being vigorously stirred.

After 30 minutes at room temperature the solution was dark yellow-green in colour, and after 1 hour golden-yellow. The solution was stirred for sixteen hours at room temperature to ensure the reaction was complete. When stirring was stopped a bright-yellow solid, and a dark brown liquor resulted. The solution was capillary filtered. The brown liquor was concentrated by evaporation of the solvent using a rapid flow of nitrogen, a slight yellow precipitate being noted and finally traces of solvent were removed under reduced pressure to produce a brown solid. The residue was re-dissolved in diethyl ether (30 ml.), and the solution filtered. A brown-yellow solid formed when the liquor was concentrated under reduced pressure. Attempts at recrystallisation of this solid in acetone resulted in gum formation. The solid was finally recrystallised from dichloromethane (20 ml.), to produce $Pt\{p\text{-}FC_6H_4NC(C_6H_5)NC_6H_4F\text{-}p\}_2$ as a mustard-brown powder. This was washed with 60/80 petroleum ether (10 ml.), before drying *in vacuo*.

Infra-red studies indicated that some product remained in the original yellow filtrate, which also gave a

positive lithium flame test, therefore further extractions were carried out to yield more product. Any attempt to precipitate the product out of solution by addition of n-pentane, hexane or toluene resulted in noticeable decomposition and precipitation of impure product.

^{1}H N.M.R. ($CDCl_3$) ppm: δ7.6, 7.0, 6.4(26) very broad.

^{19}F n.m.r.($CDCl_3$) ppm: -120.2 singlet ($CFCl_3$).

Mass spectrum: The parent ion $[^{195}Pt(DPFPBA)_2]^2$ was observed at m/e 809. Fragmentation occurred by two pathways A and B, (Section 4.3). A low intensity peak corresponding to $[^{195}Pt(DPFPBA)_2(PhCN)]^+$ was also noted at m/e 912.

Positive Ion F.A.B. Mass Spectrum: (i) glycerol mull; only weak peaks corresponding to the ligand were observed. (ii) in 2,4 diamyl phenol; the general features of the spectrum were found to be similar to that found for transition metal allyl complexes which have been studied previously by this technique[1] . Fragmentation was characterised by weak parent ions and numerous fragment ions indicating a complex breakdown pattern. The parent ion at m/e 810 corresponds to [M+1], and the peak at m/e 503 corresponds to the $[^{195}Pt(DPFBA)+1]^+$ ion. Ions were observed at m/e 309, m/e 198, and m/e 195 corresponding to $[DPFBA+1]^+$ $(PhCN_2C_6H_4F]^+$ and $[^{195}Pt]^+$ respectively. A number of other ions were observed at m/e 516, 474, 459, 443 and 389 which may be due to fragmentations of the co-ordinated ligand, or else decomposition of the complex. Decomposition is a possibility because the mull was made up in air. Neither of these two possibilities may be ruled out.

4.2.2 Reaction of $Pt(PhCN)_2Cl_2$ with [p-$Pr^iC_6H_4N(Li)C(C_6H_5)NC_6H_4Pr^i$-$p$]

Quantities used: $Pt(PhCN)_2Cl_2$ (1.180g., 2.5 mmol), DPIPBAH (1.78g., 5 mmol); diethyl ether (30 ml.).

The lithiation and reaction steps were carried out as described previously (Section 4.2.1). After 16 hours the resultant brown mixture was allowed to settle yielding a yellow solid and a brown liquor. The solution was filtered and the solvent removed *in vacuo* from the filtrate to yield a brown solid which was extracted with dichloromethane (30 ml.). After filtration the solution was reduced in volume to yield $Pt\{p\text{-}Pr^iC_6H_4NC(C_6H_5)NC_6H_4Pr^ip\}_2$, as a mustard brown solid which was recrystallised from dichloromethane.

^1H N.M.R., ($CDCl_3$) ppm: δ7.1-6.4(26) very broad, 2.7(4) very broad 1.2, 1.19, 1.1(24) multiplet broad.

Mass spectrum: the parent ion $[^{195}Pt(DPFPBA)_2]^+$ was observed at m/e 905. Fragmentation occurred through both pathway A and pathway B, (Section 4.3). A low intensity peak corresponding to $[^{195}Pt(DPIPBA)_2(PhCN)]^+$ was observed at m/e 1008.

4.2.3 Reaction of $Pt(PhCN)_2Cl_2$ with [$CH_3N(Li)C(C_6H_5)NCH_3$]:

Quantities used: $Pt(PHCN)_2Cl_2$, (1.18g; 2.5 mmol), DMBAH (0.74g; 5mmol); diethyl ether (100 ml.).

The lithiation step, and addition of reactants were carried out as described in Section 4.2.1. After 16 hours the mustard brown reaction was reduced to a yellow residue by evaporation using a vigorous flow of nitrogen. Dichloromethane (200 ml.) was added yielding a yellow solid and a

yellow liquor. The solvent extract was removed by syringe and after filtration was concentrated under reduced pressure to yield golden-yellow plates. The solid was recrystallised from dichloromethane (20 ml.) to yield $Pt\{CH_3NC(C_6H_5)NCH_3\}_2$. Further recrystallisation from toluene (60 ml.) and dichloromethane (25 ml.) were carried out.

^{1}H N.M.R. ($CDCl_3$) ppm. δ7.5(10), 2.9(12) both signals very broad. Mass spectrum: Weak peaks were observed at m/e 621 corresponding to $[^{195}Pt(DMBA)_2CN_2CH_3C_6H_5]^+$, m/e 518 corresponding to $[^{195}Pt(DMBA)_2NCH_3]^+$ and at m/e 503 corresponding to $[^{195}Pt(DMBA)_2N]^{+2}$. A strong peak was observed at m/e 489 corresponding to $[^{195}Pt(DMBA)_2]^+$. Fragmentation occurred through pathways A and B, (Section 4.3).

4.2.4 Reaction of $Pt(PhCN)_2Cl_2$ with $[C_6H_5N(Li)C(C_6H_5)NC_6H_5]$:

Quantities used: $Pt(PhCN)_2Cl_2$, (0.59g, 1.25 mmol); DPBAH (0.68g; 2.5mmol), diethyl ether (50 ml.).

The lithiation step and the addition of reactants were carried out as described previously (Section 4.2.1). After 16 hours a yellow mixture resulted, which was reduced to a yellow solid using a vigorous flow of nitrogen. Three extractions with toluene 100 ml., 60 ml. and 60 ml. were separately filtered. Evaporation of the toluene using a nitrogen stream yielded yellow powders which were found to be similar by i.r. spectroscopy. They were combined and recrystallised from dichloromethane (20 ml.). The product $Pt(DPBA)_2$ consisted of yellow microcrystalline needles in a powder.

^{1}H N.M.R. ($CDCl_3$) ppm: δ7.0, 6.9, 6.8, 6.7 (30) very broad. Mass spectrum: the parent ion $[^{195}Pt(DPBA)_2]^+$ was observed at m/e 735. Fragmentation occurred by both pathway A and pathway B (Section 4.3).

4.2.5 Reaction of $Pt(PhCN)_2Cl_2$ with [*p*-$CH_3C_6H_4N(Li)C$-$C_6H_5)NC_6H_4CH_3$-*p*].

Quantities used: $Pt(PhCN)_2Cl_2$ (0.295 g; 0.625 mmol), DPTBAH (0.375g; 1.25 mmol), tetrahydrofuran (50 ml.).

The lithiation step and addition of reactants was carried out as described previously (Section 4.2.1). After 16 hours the solution was golden-yellow in colour. Complete solvent removal was achieved using a vigorous stream of nitrogen, and the solid formed was extracted with dichloromethane (100 ml.). The filtered solution was placed in a freezer (-16°C) overnight, and a small quantity of fluffy yellow solid was deposited. The solid which had a positive lithium flame test was removed by filtration. The liquor was concentrated under reduced pressure, and placed in the freezer for several days. A yellow-brown solid was deposited which was separated and recrystallised from dichloromethane to yield $Pt(DPTBA)_2$ as a yellow powder which was washed with toluene (30 ml.) before drying.

^{1}H N.M.R. ($CDCl_3$) p.p.m. δ7.2-6.4 (26) very broad, 2.2(12)broad. Mass spectrum: The parent ion $[^{195}Pt(DPTBA)_2]^+$ was observed at m/e 793. Fragmentation occurred by both routes A and B (Section 4.3).

4.2.6 Reaction of $Pt(PhCN)_2Cl_2$ with $[C_6H_5N(Li)C(CH_3)NC_6H_5]$

Quantities used: $Pt(PhCN)_2Cl_2$ (1.18g., 2.5mmol), DPAAH (1.05g.; 5mmol), tetrahydrofuran (60 ml.).

Lithiation and addition of reactants was carried out in the manner described previously (Section 4.2.1). After 16 hours the reaction solution was orange in colour. Dichloromethane (20 ml.) and n-pentane (50 ml.) were added to the reaction mixture and it was cooled to $-16^{o}C$. The solution yielded a mustard yellow solid which was separated by filtration. The mother liquor was reduced in volume *in vacuo* to 40 ml., n-pentane (40 ml.) was added and the mixture cooled to $-16^{o}C$. More mustard brown solid was produced, which was filtered and washed with n-pentane (20 ml.). The process was repeated again to increase yield. The resultant mustard-brown powders were recrystallised from dichloromethane (35 ml.) to yield $Pt(DPAA)_2$.

^{1}H. N.M.R. ($CDCl_3$) p.p.m. 7.0(20 broad 1.8(6).

Mass spectrum: The parent ion $[^{195}Pt(DPAA)_2]^+$ was observed at m/e 613. Fragmentation occurred through path B (Section 4.3).

4.2.7 Reaction of $Pd(PhCN)_2Cl_2$ with $[C_6H_5N(Li)C(C_6H_5)-N-C_6H_5]$:

Quantities used $Pd(PhCN)Cl_2$ (0.9575g.; 2.5mmol), DPBAH (1.36g.; 5mmol), diethyl ether (80 ml.).

The procedure used was as described previously (Section 4.2.1). On warming to room temperature the solution became orange in colour, and blood red after 8 hrs. The solvent was removed by a vigorous stream of nitrogen to yield a red-orange solid. After extraction with dichloromethane (70 ml.) and filtering the solution, cooling to -16^{o} produced red micro-crystals of $Pd_2(DPBA)_4$ which were separated and washed with hexane (20 ml.). The process was repeated after evaporation of approximately one-third of the solvent under reduced pressure, to yield further product. Further recrystallisations from both dichloromethane and chloroform yielded the same red product. It was noted that over long periods (weeks) in both chlorinated solvents and hydrocarbons decomposition of the product occurred and metal was one of the decomposition products. Toluene was also found useful for the extraction and recrystallisation stages, the limiting factor being the solubility in toluene which was less than in dichloromethane.

^1H N.M.R. ($CDCl_3$) p.p.m. 6.8 (very broad).

Mass spectrum: The parent ion $[^{106}Pd_2(DPBA)_4]^+$ was observed at m/e 1292. Fragmentation occurred by pathways A and B, (Section 4.3).

4.2.8 Reaction of $Pd(PhCN)_2Cl_2$ with [*p*-$FC_6H_4N(Li)C(C_6H_5)NC_6H_4F$-*p*]

Quantities used: $Pd(PhCN)_2Cl_2$ (0.9575g.; 2.5mmol), DPFPBAH (o.54g.; 5mmol), diethyl ether (80 ml.).

The procedure used was identical to that described in Section 4.2.7, the final product, red $Pd_2(DPFPBA)_4$ being recrystallised from dichloromethane (40 ml.).

^1H N.M.R. ($CDCl_3$): p.p.m. δ7.0, 6.6, 6.4 (26) very broad.

^{19}H N.M.R. ($CDCl_3$) p.p.m. -120.1 singlet ($CFCl_3$ ref.).

Mass spectrum: the parent ion $[^{106}Pd_2(DPFPBA)_4]^+$ was observed at m/e 1440. Fragmentation occurred through pathway A, (Section 4.3).

4.2.9 Reaction of $Pd(PhCN)_2Cl_2$ with [$CH_3N(Li)CH_2NCH_3$]

Quantities used: $Pd(PhCN)_2Cl_2$ (0.9575 g.; 2.5mmol), DMBAH (0.74g.; 5mmol), tetrahydrofuran (50 ml.).

The reaction was analogous to that in Section 4.2.7, except that the final colour of the reaction mixture after 16 hours was yellow. The yellow product $Pd_2(DMBA)_4$ was recrystallised from dichloromethane (35ml.).

Mass spectrum: the parent ion $[^{106}Pd_2(DMBA)_4]^+$ was observed at m/e 800. Fragmentation occurred through both pathways A and B (Section 4.3).

4.2.10 Reaction of $Pd(PhCN)_2Cl_2$ with [*p*-$Pr^iC_6H_4N(Li)C(C_6H_5)NC_6H_4Pr^i$-*p*]

Quantities used: $Pd(PhCN)_2Cl_2$ (0.9575g; 2.5mmol), DPIPBAH (1.78g.; 5mmol).

The reaction was carried out as in Section 4.2.7, the blood-red product $Pd_2(DPIPBA)_4$ being recrystallised from dichloromethane (150 ml.).

^1H N.M.R. ($CDCl_3$), p.p.m. δ6.9, 6.0 (52) very broad, 2.1(8) very broad, 1.2, 1.1 (24) doublet (very broad).

Mass spectrum: The parent ion at m/e 1632 corresponding to $[^{106}Pd_2(DPIPBA)_4]^+$ was not observed. Fragmentation occurred through pathway A (Section 4.3).

4.2.11 Reaction of $Pd(PhCN)_2Cl_2$ with [*p*$CH_3C_6H_4N(Li)C(C_6H_5)NC_6H_4CH_3$-*p*]

Quantities used: $Pd(PhCN)_2Cl_2$ (0.9575g.; 2.5mmol), DPTBAH (1.5g.; 5mmol), tetrahydrofuran (50 ml.).

The reaction conditions were analogous to those given in Section 4.2.8. The red powder produced was slowly recrystallised from dichloromethane (20ml.) at -16°C. Blood red amorphous crystals of $Pd_2(DPTBA)_4$ resulted.

^1H N.M.R. ($CDCl_3$) p.p.m. δ6.9(52) very broad, 2.2(24) very broad.

Mass spectrum: the parent ion $[^{106}Pd_2(DPTBA)_4]^+$ was observed at m/e 1408. The fragmentation occurred through both path; way A and pathway B (Section 4.3).

4.2.12 Reaction of anhydrous $NiCl_2$ (0.3 $C_4H_{20}O_2$) with $[C_6H_5N(Li)C(C_6H_5)NC_6H_5]$

Quantities used: $NiCl_2$ (0.7831g; 5 mmol), DPBAH (2.72g; 10 mmol) monoglyme (100 ml.).

The procedure used was identical to that described in Section 4.2.1. On warming to room temperature the solution became yellow-green in colour, then dark green after 14 hours. Evaporation of the monoglyme solution using a nitrogen stream yielded a green powder, which was extracted with toluene (140 ml.). The solution was filtered and reduced to a green solid *in vacuo*, the residue was nickel chloride. The green solid, identified as crude $Ni_2(DPBA)_4$, decomposed very rapidly when exposed to air, and even under *vacuo* at room temperature slight decomposition occurred. The product was dissolved in tetrahydrofuran and placed on a 20mm.X150mm. silica column (Kieselgel 60 Brackmann 2-3), cooled by means of a water-jacket. At the top of the column the solvent front was green, at the bottom of the column it became brown. The brown eluent was reduced to the solid *in vacuo*, and recrystallised from dichloromethane (20 ml.) after filtration. The brown solid produced contained metal and was clearly a decomposition product. Washing with hexane (80 ml.) yielded a small amount of nickel chloride.

Mass spectrum: the parent ion $[^{59}Ni_2(DPBA)_4]^+$ was observed at m/e 1198. Further fragmentation followed paths A and B (Section 4.3).

4.2.13 Reaction of anhydrous $NiCl_2$ (0.3 $C_4H_{10}O_2$) with [*p*.$FC_6H_4N(Li)C(C_6H_5)NC_6H_4F$-*p*).

Quantities used: $NiCl_2$ (1.178g; 7.5 mmol), DPFBAH (4.62g; 15mmol), monoglyme (150 ml.).

The procedure used was identical to that described in Section 4.2.12. The solution was green-brown in colour after 48 hours. The solution was reduced in volume using a vigorous flow of nitrogen to produce a green-brown solid. The last traces of solvent were removed under reduced pressure. The solid was extracted with toluene (120 ml.), the solution filtered and reduced in volume *in vacuo*. Green $Ni_2(DPFPBA)_4$ was isolated as a powder which was recrystallised from tetrahydrofuran (80 ml.). Yellow nickel chloride was present in the filtration residue.

^1H N.M.R. (CD_2Cl_2) ppm.: δ6.91, 6.59, 6.23, (52), 3.76 (16) [THF solvate], 2.8 (16) [THF solvate].

^{19}F N.M.R.(CD_2Cl_2) p.p.m.-119.8 ($CFCl_3$ ref.).

Mass spectrum: the parent ion was not observed, the highest ion observed at m/e 1039, corresponding to $[^{59}Ni_2(DPFPBA)_3]^+$. Fragmentation only occurred *via* pathway A (Section 4.3).

4.2.14 Reaction of anhydrous $NiCl_2$ (0.3 $C_4H_{10}O_2$) [*p*-Pr^iN-$LiC(C_6H_5)NC_6H_4Pr^i$-*p*].

Quantities used: $NiCl_2$ (1.5662g; 10mmol), DPIPBAH (7.12g; 20 mmol), monoglyme (100 ml.).

The procedure used was identical to that described in Section 4.2.12. The dark green solution was reduced by a

vigorous nitrogen stream to form a green solid, the final traces of solvent being removed *in vacuo*. The green solid was extracted with toluene (100 ml.), the solution filtered and cooled to -16°C. for several hours. The green product $Ni_2(DPIPBA)_4$ was collected and dried *in vacuo*. In the presence of moisture a metallic grey decomposition product. Significant decomposition occurred at -16°C in the solid state and under *vacuo* over long periods (days).

Mass spectrum: the parent ion was not observed. The highest mass observed at m/e 1021 corresponded to $[^{59}Ni_2(DPIPBA)_2NC\text{-}PhNC_6H_4]^+$. Fragmentation occurred by both pathway A and pathway B (Section 4.3.1).

4.2.15 Reaction of anhydrous $NiCl_2(0.3\ C_4H_{10}O_2)$ with $[p\text{-}CH_3\text{-}C_6H_4N(Li)C(C_6H_5)NC_6H_4CH_3\text{-}p]$

Quantities used: $NiCl_2$(0.7831g; 5 mmol), DPTBAH (3.0g; 10 mmol) monoglyme (150 ml.).

The procedure used was identical to that described in Section 4.2.12. After 18 hours the dark green solution was reduced using a vigorous nitrogen stream, the last traces of solvent being removed under reduced pressure. The green solid was extracted with toluene (150 ml.), the solution filtered and reduced to yield green $Ni_2(DPTBA)_4$ *in vacuo*. Since small amounts of nickel chloride were clearly visible in the product, a further toluene extraction and filtration was carried out. Even under *vacuo* the green product decomposed rapidly, grey metal particles and brown powder being formed. An attempt was made to purify the solid by passing a solution of the green

solid down an alumina column (Beckmann grade 1) 20mm X 200mm, and eluting with dichloromethane. Green and brown bands were developed but partial decomposition occurred whilst the solvent was removed under *vacuo*.

Mass spectrum: the parent ion was not observed. The highest mass observed at m/e 1015 corresponded to $[^{59}Ni_2(DPTBA)_3]^+$. Fragmentation followed both pathway A and pathway B (Section 4.3.). The brown decomposition product showed only traces of ions which were observed for the green $Ni_2(DPTBA)_4$ solid.

4.2.16 Reaction of anhydrous $NiCl_2$ with $[C_6H_5N(Li)C(CH_3)NC_6H_5]$

Quantities used: $NiCl_2$ (1.5662g; 10 mmol), DPAAH (4.2g; 20 mmol), monoglyme (150 ml.).

The procedure used was identical to that described in Section 4.2.12. After 18 hours the dark green solution was filtered and the solvent removed *in vacuo*. Yellow nickel chloride was the main constituent of the filtration residue. White and grey solids were also noted in the dark green solid which was extracted with toluene (150 ml.) yielding a dark green solution. The solution was filtered, concentrated *in vacuo*. and then placed in the freezer (-16^oC) for 48 hours. Yellow nickel chloride was again the main constituent of the solid which separated. After 48 hours long green needles of $Ni_2(DPAA)_4$ were observed. The liquor was removed by syringe concentrated *in vacuo* and placed in the freezer to yield a second crop of crystals. The needles decomposed to a grey, green and white powder on warming to room temperature.

Mass spectrum: the parent ion $[^{59}Ni_2(DPAA)_4]^+$ was observed at m/e 954. Fragmentation occurred by pathway A only, (Section 4.3).

4.3 Mass Spectra

Daughter ions observed for the bis-amidino complexes show two fragmentation pathways. The first, pathway A, involves loss of amidino ligand ions as a whole and metal ions. The second pathway B involves fragmentation of the ligand whilst it is still co-ordinated to the metal. Pathway A is described in Figure 4.1, and the relevant data tabulated in Tables 4.1 and 4.2.

Pathway A is the most favoured fragmentation route (Fig.4.1) and many of the transitions are supported by metastable peaks. The pathway follows two routes, the first involving a dimetallic species, the second breakdown of the dimer to the monomer and finally to the ligand ion. Only monomer breakdown was observed for the platinum (II) species. The ligand ion fragmentation pattern was found to be very similar to that found for the uncoordinated ligand. The second pathway B involved fragmentation of the ligand whilst it was still co-ordinated to the metal. It is a less favoured pathway, and appears to be fairly random in its occurrence, hence examples of the ions formed are described in Table 4.3.

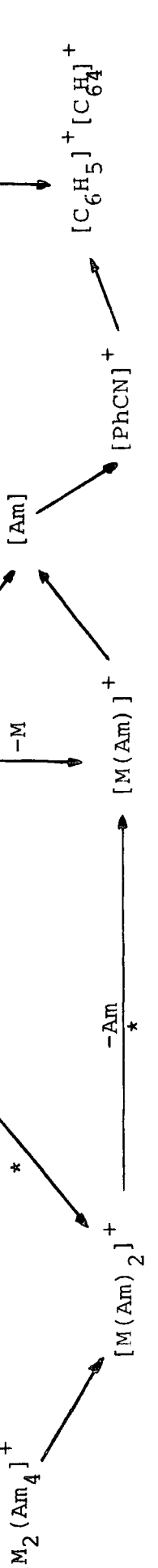


Figure 4.1 Postulated Mass Spectral Fragmentation Scheme for Bis-amidino Complexes of Pt(II), Pd(II) and Ni(II) (Pathway A).

* indicates transition supported by a metastable.

TABLE 4.1 Mass Spectral Fragments for Bis-amidino Pt(II) Complexes

Scheme A	AMIDINO LIGAND (M/e)					
Fragments	DPFPBA	DPIPBA	DMBA	DPBA	DPTBA	DPAA
$Pt(Am)_2$	809	905	489	737	793	613
Pt(Am)	502	550	342	466	494	404
Am	307	355	147	271	299	209
R´´NCR´	198	222	118	180	194	118
PhCN	103	103	103		103	103
C_6H_4-R´´´	95	119		77	91	77
C_6H_5	77	77	77	77	77	77
C_6H_4	76	76	76	76	76	76
	m^* 127.7 (307-198)	m^* 138.8 (355-222)	m^* 50.2 (118-77)		m^* 125.8 (299-194)	m^* 50.2 (118-77)
	m^* 60.8 (95-76)	m^* 63.8 (222-119)			m^* 42.7 (194-91)	
		m^* 57.5 (103-77)				
		m^* 39.8 (355-119)				

TABLE 4.2 Mass Spectral Fragments for Dimeric Bis-amidino Pd(II) and Ni(II) Complexes

Scheme A	AMIDINO LIGAND (m/e)											
Fragments	DPFPBA		DPIPBA		DMBA		DPBA		DPTBA		DPAA	
	Pd	Ni	Pd	Ni	Pd	Ni	Pd	Ni	Pd	Ni	Pd	Ni
$M_2(Am)_4$	1440				800		1296	1202	1408			954
$M_2(Am)_3$	1133	1039	1277				1025	931		1015		
$M_2(Am)_2$	826	732	922	828	506		754	660	810	716		536
$M(Am)_2$	720	673	816	769	400		648	601	704	657		477
$M_2(Am)$			567				482	389				
M(Am)	413	366	461	414	253		377	330	405	358		268
Am	307	307	355	355	147		271	271	299	299		209
R´´NCR´	198	198	222	222	118		180	180	194	194		118
PhCN	103	103	103	103	103		103	103	103	103		103
C_6H_4R'''	95	95	119	119			77	77	91	91		
C_6H_5	77	77	77	77	77		77	77	77	77		77
C_6H_4	76	76	76	76	76		76	76	76	76		76
	m^* 127.7	m^* 127.7	m^* 999.2	m^* 138.5	m^* 50.2		m^* 810.7			m^* 125.8		
	(307-198)	(307-198)	(1632-1277)	(355-222)	(118-77)		(1296-1425)			(299-194)		
	m^* 60.8	m^* 60.8	m^* 138.8				m^* 56.9			m^* 42.7		
	(95-76)	(95-76)	(365-222)				(754-698)			(194-91)		
		m^* 45.8	m^* 63.8				m^* 219.3					
		(198-95)	(222-119)				(648-377)					
			m^* 57.7				m^* 119.6					
			(103-77)				(271-180)					

KEY: R´ = Ph in all cases except DPAA, where R´ = CH_3. R´´ = C_6H_4-F, $C_6H_4Pr^i$, CH_3-Ph, C_6H_4-CH_3, Ph respectively. R´´´ = F, Pr^i, -, H, CH_3.H respectively.

TABLE 4.3 Mass Spectral Fragments Involving Ligand Breakdown Whilst Still Coordinated to the Metal

(a) $Pt(DPFPBA)_2$: m/e 714 corresponding to $[^{195}Pt(Am)N_2C(Ph)-C_6H_4-F]^+$;

m/e 611 corresponding to $[^{195}Pt(Am)NC_6H_4-F]^+$.

(b) $Pt(DPIPBA)_2$: m/e 816 corresponding to $[^{195}Pt(Am)N_2-(C_6H_4Pr^i)_2]^+$;

m/e 709 corresponding to $[^{195}Pt(Am)N_2C-C_6H_4Pr^i]^+$;

m/e 461 corresponding to $[^{195}PtN_2(C_6H_4Pr^i)_2]^+$

(c) $Pt(DMBA)_2$: m/e 518 corresponding to $[^{195}Pt(DMBA)_2NCH_3]^+$;

m/e 503 corresponding to $[^{195}Pt(DMBA)_2N_2]^+$;

m/e 474 corresponding to $[^{195}PtCC_6H_5CH_3]^+$;

m/e 382 corresponding to $[^{195}Pt(DMBA)N_2C]^+$;

m/e 313 corresponding to $[^{195}PtNCC_6H_5CH_3]^+$.

(d) $Pt(DPBA)_2$: m/e 660 corresponding to $[^{195}M(Am)N_2C-(C_6H_5)_2]^+$;

m/e 375 corresponding to $[^{195}PtPhNCPh]^+$.

(e) $Pt(DPBA)_2$: m/e 660 corresponding to $[^{195}Pt(Am)N_2C-(C_6H_5)_2]^+$;

m/e 389 corresponding to $[^{195}PtN_2C(C_6H_5)_2]^+$.

TABLE 4.3 (contd...)

(f) $Pt(DPTBA)_2$: M/e 673 corresponding to $[^{185}Pt(Am)NC-C_6H_5C_6H_4]^+$;
m/e 403 corresponding to $[^{195}PtN_2C-C_6H_5C_6H_4CH_3]^+$.

(g) $Pt(DPAA)_2$: m/e 459 corresponding to $[^{195}Pt(DPAA)N_2-CCH_3]^+$;
m/e 313 corresponding to $[^{195}PtNPhCH_3]^+$.

(h) $Pd_2(DPBA)_4$: m/e 688 corresponding to $[^{106}Pd(Am)_2N_2C]^+$.

(i) $Pd_2(DPFPBA)_4$: no peaks observed.

(j) $Pd_2(DMBA)_4$: m/e 161 corresponding to $[^{106}PdN_2CCH_3]^+$.

(k) $Pd_2(DPIPBA)_4$: no peaks observed.

(l) $Pd_2(DPTBA)_4$: no peaks observed.

(m) $Ni_2(DPBA)_4$: m/e 447 corresponding to $[^{59}Ni(DPBA)N_2CPh]^+$;
m/e 433 corresponding to $[^{59}Ni(DPBA)NCPh]^+$.

(n) $Ni_2(DPFPBA)_4$: m/e 658 corresponding to $[^{59}Ni(DPFPBA)N_2C-C_6H_5C_6H_4C_6H_4-F]^+$;
m/e 456 corresponding to $[^{59}Ni(DPFBA)NC_6H_4]^+$.

(o) $Ni_2(DPIPBA)_4$: m/e 918 corresponding to $[^{59}Ni_2(DPIPBA)_2-NC_6H_4]^+$;
m/e 573 corresponding to $[^{59}(DPIPBA)NCNC_6H_4-Pr^i]^+$.

(p) $Ni_2(DPTBA)_4$: m/e 463 corresponding to $[^{59}Ni(DPTBA)N-C_6H_4CH_3]^+$;
m/e 448 corresponding to $[^{59}Ni(DPTBA)N-C_6H_4]^+$.

(q) $Ni_2(DPAA)_4$: no peaks observed.

Interpretation of high mass data was aided by computer simulations.

4.4 Analytical Results

The results obtained are consistent with the formulation $[M(Am)_2]$, (Table 4.4). The unstable nickel complexes were analysed as soon as possible after synthesis of pure product. Nickel metal analysis provided only unreliable results because the samples tended to decompose in both the gelatin and the glass tubes used to hold the samples.

TABLE 4.4 Analytical Results

Compound	%Yield	mp.°c (dec)	metal %	C %	N %	H %	Fluorine %
$Pt(DPFPBA)_2$	64.3	238d	23.77 (24.1)	56.64 (56.38)	7.27 (6.92)	3.97 (3.21)	9.21 (9.39)
$Pt(DPIPBA)_2$	28.7	122d	20.7 (21.54)	62.32 (66.31)	6.09 (6.18)	5.92 (5.96)	
$Pt(DMBA)_2 C_6H_5CH_3$	14.7	116d	30.12 (33.56)	52.22 (51.64)	9.71 (9.63)	5.78 (5.16)	
$Pt(DPBA)_2$	51.3	177d	24.54 (26.45)	61.81 (61.88)	7.41 (7.59)	4.54 (4.07)	
$Pt(DPTBA)_2$	38.3	171d	23.33 (24.59)	63.74 (63.57)	6.95 (7.06)	5.83 (4.79)	
$Pt(DPAA)_2 (CH_2Cl_2)$	22.8	136d	29.4 (27.94)	50.48 (49.88)	8.03 (8.02)	(4.02) (4.01)	
$Pd_2(DPBA)_4$	64.2	133d	16.79 (16.4)	71.31 (70.34)	8.34 (8.63)	3.88 (4.62)	
$Pd_2DPFPBA)_4$	78.9	246	14.70 (14.76)	65.93 (63.32)	7.85 (7.77)	4.32 (3.61)	11.52 (10.54)
$Pd_2(DMBA)_4$	23	177d	23.17 (26.56)	54.91 (53.17)	13.59 (13.98)	5.86 (5.49)	
$Pd_2(DPIPBA)_4$	80.4	118d	12.78 (13.02)	75.18 (73.51)	6.56 (6.86)	6.98 (6.61)	
$Pd_2(DPTBA)_4$	89.3	122d	15.39 (15.10)	69.17 (71.57)	7.54 (7.94)	6.12 (5.39)	
$Ni_2(DPBA)_4$	78.9	134d	- -	75.50 (75.92)	8.52 (9.32)	5.16 (4.99)	
$Ni_2(DPFPBA)_4$ 4 T.H.F.	62.3	138d	- -	68.88 (67.61)	6.72 (6.85)	3.84 (5.14)	8.91 (9.1)
$Ni_2(DPIPBA)_4$	89.1	70d	- -	78.82 (78.07)	7.42 (7.78)	8.05 (7.02)	
$Ni_2(DPTBA)_4$	-	-	-	77.44 (76.76	7.97 (8.52)	6.47 (5.78)	
$Ni_2(DPAA)_4$	-	140d	- -	74.98 (70.50)	11.48 (11.74)	5.77 (5.45)	

Found (calculated)

THERMOGRAMS for BIS-AMIDINO PLATINUM(II) COMPLEXES

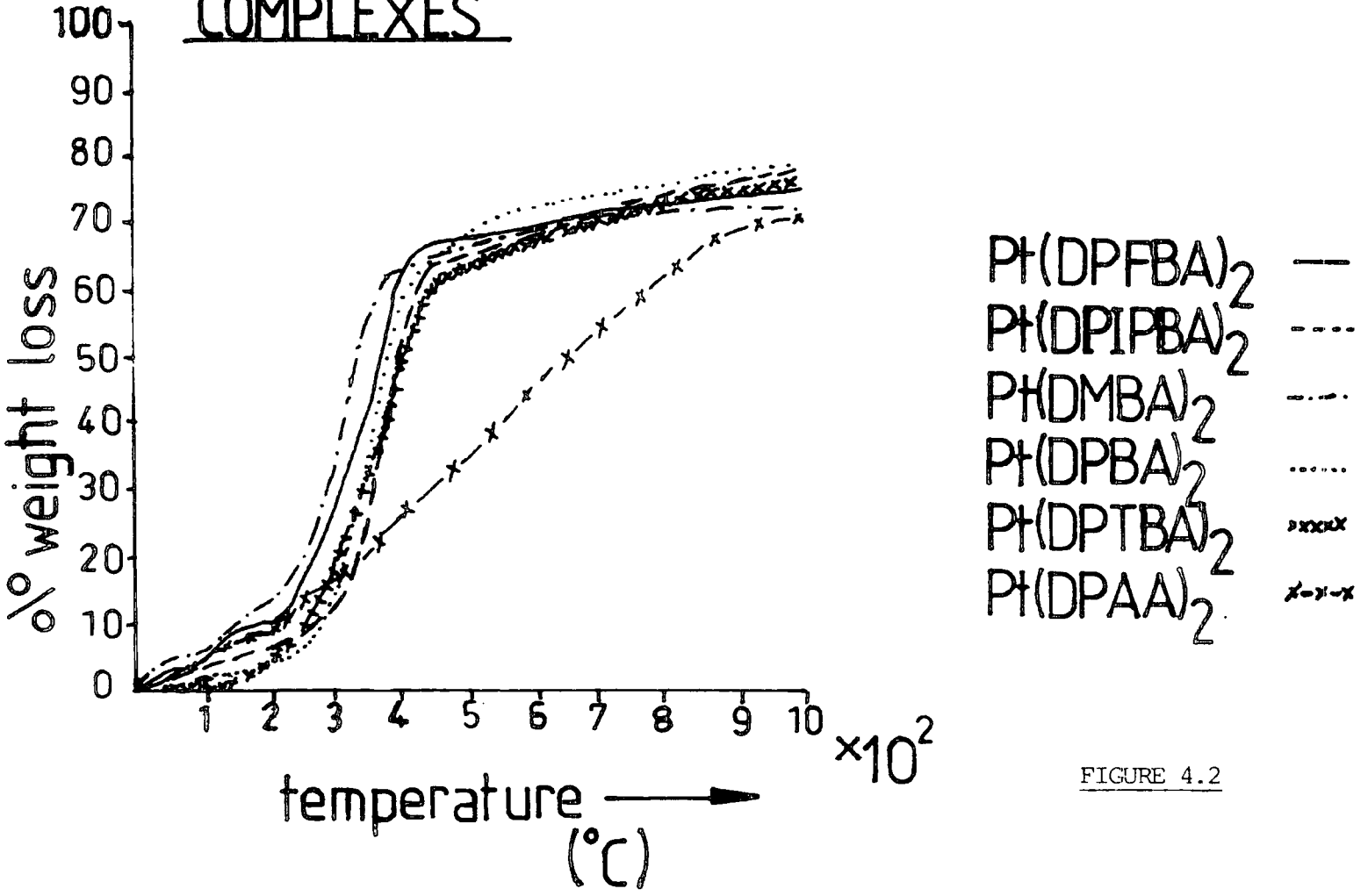


FIGURE 4.2

4.5 Thermogravimetric Analysis

The platinum complexes were analysed under nitrogen over the temperature range 0-1000°C. The traces are shown in Figure 4.2. The thermograms all show ill defined transitions, many of which could not be assigned to characterisable decomposition steps (Table 4.5).

The final residues were in agreement with those expected for the theoretical platinum contents of the complexes. The residues were analysed by atomic absorption spectrophotometry, which showed they were platinum metal. The solvated complexes show loss of solvent, but the transitions are ill defined and only approximate to the values expected: $Pt(DMBA)_2C_6H_5CH_3$ theoretical % weight loss for loss of $C_6H_5CH_3$ = 15.8%, found *c.a.* 12%; $Pt(DPAA)CH_2Cl_2$ theoretical % weight loss for loss of CH_2Cl_2 = 12%, found = 11%.

The penultimate transition may, in all cases, except $Pt(DPAA)_2$, be attributed to the presence of a PtN-(R) species, *e.g.* $Pt(DPFPBA)_2$, % weight loss found 66 (theoretical 62.4); (R) = NC_6H_4-F; $Pt(DPIPBA)_2$, 64(63.2); $Pt(DMBA)_2$, 62(61.4); $Pt(DPBA)_2$, 63(61.9); $Pt(DPTBA)_2$, 61(62.2).

In the case of $Pt(DPAA)_2$, the % weight loss of 43% may be attributed to the loss of CH_2Cl_2 and (DPAA) leaving a residue of Pt(DPAA), (Found 57%(58%)).

TABLE 4.5 Thermogravimetric Analysis Transitions and Temperatures

Complex	% wt. loss	Temperature range of transition, °C
$Pt(DFPBA)_2$	0 - 10	0 - 158
	0 - 64	158 - 476
	0 - 86.5 (residue = 23.5)	476 - 923
$Pt(DPIPBA)_2$	0 - 4	0 - 181
	0 - 64	181 - 420
	0 - 77.6 (residue = 22.4)	420 - 870
$Pt(DMBA)_2$	0 - 5	0 - 94
$C_6H_5CH_3$	0 - 12	94 - 170
	0 - 62	170 - 371
	0 - 72 (residue - 28)	371 - 954
$Pt(DPBA)_2$	0 - 1.5	0 - 120
	0 - 6	120 - 226
	0 - 63	226 - 391
	0 - 77.9 (residue - 22.1)	391 - 876
$Pt(DPTBA)_2$	0 - 2	0 - 94
	0 - 61	94 - 448
	0 - 73.5 (residue = 26.5)	448 - 931
$Pt(DPAA)_2$	0 - 11	0 - 193
CH_2Cl_2	0 - 18	193 - 270
	0 - 43	270 - 611
	0 - 69 (residue = 31.0)	611 - 899

4.6 Infra-red Absorption (Table 4.6)

Significant changes occur in the R´NC(R)NHR´ spectrum in the range 1650-1200 cm^{-1} when complexes are formed, and these may be rationalised in terms of the vibrations described in Prevorsek[2].

The bands in the *ca.* 1640 - 1600 cm^{-1} region were assigned to ν_{asym}(NCN) vibrations and designated amidine I. The strong bands *ca.* 1615-1588cm^{-1} region were assigned to ν_{asym}(C=N) and again designated amidine-I in the parent amidines. On complexation the ν_{asym}(NCN) bands were considerably reduced in intensity, and in many cases were no longer detectable. The ν_{asym}(C=N) band intensity was affected to a slight degree.

A number of bands in the region *ca.* 1390-1520 cm^{-1} are considerably reduced in intensity and they may be tentatively assigned to the Amidine II vibration, described by Prevorsek[2] as consisting of a complicated mixture of $\nu_{C=N}$ and δN-H vibration.

The Amidine-III band *ca.* 1240-1400 cm^{-1} is also considerably affected by coordination, either being considerably shifted or reduced in intensity. The vibration is described as a complicated mixture of ν(C=N), δ(NH) and ν(RCH-C) vibrations.

The complicated nature of amide (3) and thioamide (4) spectra where many absorption bands cannot be adequately described by the displacement of two atoms only have been described by the momenclature amide-I, thioamide-I *etc.* both in organic and co-ordination chemistry. It appears that the use of amidine-I, -II, *etc.* based on Prevorsek's[2]

work may be useful in a similar manner. The evidence for coordination is obvious from the i.r. data described; however the actual mode of co-ordination is more difficult to determine. There is a lowering of the ν_{sym}(NCN) frequency, and/or its intensity in the complexes in a similar manner to that found in benzamidino-rhenium complexes which are known to contain chelate bidentate ligands. Monodentate palladium formamidine complexes [6], also exhibit similar ν_{asym}(NCN) absorptions, but lack the strong bands *ca.* 1590 cm^{-1} observed for the complexes prepared in this study. Thus the i.r. evidence indicates a bidentate mode of bonding, which may be either chelating or bridging in nature; however, the data is not totally conclusive. Similar problems with bonding mode assignments or the basis of i.r. measurements have been found for the related 1,3 diaryltriazenido ligands[7]. The ν_{asym} (NCN) vibration appears at a slightly higher frequency in the platinum than the palladium complexes, the exception being $Pt(DMBA)_2$ and $Pd_2(DMBA)_4$ which have analogous spectra.

The N-H vibrations of the parent amidines are as expected absent in the spectra of the complexes.

The M-N vibrations, because of their weak intensities, are very difficult to assign; however in a M-N σ-bonded system, as here, the vibrations would be expected to appear between 300 and 200 cm^{-1}. A prime candidate for this is a very weak band at *ca.* 270 cm^{-1} which appears in a number of the complexes studied.

TABLE 4.6 A Comparison of the i.r. Absorptions in the Region 1700-1200 cm^{-1} of the Bis-amidino complexes and their parent amidines (nujol/hexachlorobutadiene mulls).

Amidine used	Parent Amidine	Metal		
		Pt	Pd	Ni
	frequency cm^{-1}			
DPAAH	1624 v.s.			1625 m.
	1580 v.s.	1590 v.s.		1590 s.
	1525 v.s.			1530 v.s.
	1485 m.	1480 m.		1480 v.s.
	1440 m.	1420 m.		1410 s.
	1370 m.	1330 v.w.		1330 w.
	1240 m.sh.	1260 w.		1250 w.
				1220 m.
	1218 s.	1210 w.		1210 w.sh.
DMBAH	1651 v.s.			
	1635 m.sh.	1615 v.s.	1615 v.s.	
		1560 m.sh.	1560 m.br.	
	1500 s.		1500 w.	
	1490 m.			
	1450 m.	1440 w.	1470 m.	
	1385 m.			
	1370 s.	1370 w.		
	1300 m.	1260 w.	1260 m.	
	1200 v.w.		1200 v.w.	
DPBAH	1630 s.h.			
	1621 s.	1621 w.	1603 m.	1621 m.
	1589 v.s.	1589 s.		1590 s.
	1575 s.	1580 m.	1570 s.	1575 m.

TABLE 4.6 (Contd....)

Amidine used	Parent Amidine	Metal		
		Pt	Pd	Ni
		frequency cm^{-1}		
DPBAH	1530 v.s.	1530 s.		1530 v.s.
	1490 s.sh.	1490 m.		1490 v.s.
	1470 s.	1470 m.	1470 m.	
	1440 s.	1440 m.	1420 s.br.	1440 s.
	1330 s.	1330 m.	1300 w.	1330 m.
	1240 w.		1275 w.	1260 w.
			1270 w.	
	1220 s.	1220 m.	1210 m.	1220 m.
DPTBAH	1620 v.s.	1620 w.		1620 s.
	1590 v.s.	1590 m.	1590 s.	1590 v.s.
	1585 v.s.		1570 s.	1578 s.
	1520 v.s.			1520 v.s.
	1500 v.s.	1500 v.s.	1500 v.s.	1500 v.s.
	1450 m.	1450 w.		1430 s.
	1400 m.	1400 w.	1400 v.w.	1400 m.
	1330 v.s.	1330 w.		1330 m.
	1300 m.sh.			1290 w.
		1260 w.	1260 w.	1260 w.
	1220 v.s.	1220 m.	1215 m.	1220 s.
DPFPBAH	1624 s.			1620 m.
	1615 s.			
	1600 v.s.	1600 m.		1595 s.
	1590 v.s.		1580 m.br.	1580 m.
	1571 w.	1560 v.w.		
	1530 v.s.	1530 v.w.		1530 v.s.

TABLE 4.6 (contd....)

Amidine used	Parent Amidine	Metal		
		Pt	Pd	Ni
		frequency cm^{-1}		
DPFPBAH	1495 v.s.	1500 v.s.	1490 s.	1495 v.s.
		1470 m.sh.		
	1440 m.	1430 w.	1430 m.	
	1400 m.			1400 s.
	1340 m.	1310 w.		1340 m.
	1290 w.			1290 w.
		1270 w.		1260 m.
		1230 v.s.	1225 s.	1230 v.s.
	1204 v.s.	1204 v.s.	1200 m.	1205 v.w.
DPIPBAH	1620 s.		1600 m.sh.	1620 m.
	1592 v.s.	1592 s.	1590 m.	1590 m.
	1580 s.	1570 s.	1570 m.	1578 m.
	1532 v.s.			
	1515 s.	1515 v.s.	1500 s.	1500 s.
	1460 m.	1460 m.		1460 s.
	1418 s.	1420 m.	1420 w.	1430 m.
	1380 m.	1380 v.w.	1380 v.w.	
	1340 s.	1340 w.	1335 v.w.	1380 w.
		1320 v.w.		
	1300 w.	1300 v.w.	1302 v.w.	1300 w.
	1278 w.	1280 v.w.	1289 v.w.	1290 v.w.
			1260 w.	1260 w.
	1230 m.	1220 v.w.	1215 w.	1218 m.

Key: s = strong, m = medium, w = weak, v = very, sh = shoulder.

TABLE 4.7 Possible M-N vibrations for $M_n(Am)_n$ (n = 1 or 2) Complexes

Complex	ν cm^{-1}
$Pt(DMBA)_2$	270
$Pt(DPIPBA)_2$	268
$Pt(DPFPBA)_2$	270
$Pd_2(DPBA)_4$	260
$Pd_2(DPFPBA)_4$	262
$Pd_2(DPTBA)_4$	255
$Ni_2(DPIPBA)_4$	280
$Ni_2(DPBA)_4$	270

The nickel complexes show the presence of decomposition products in their spectra because of their sensitivity to thermal and aerial oxidation. The N-H region of the spectrum indicates free or possibly monodentate amidines present, as does the 1700-1200 cm^{-1} region (Table 4.6). Many of the complexes showed a brown colouration in their originally green mulls after a few minutes.

4.7 Molecular Weights

These were determined in benzene by cryoscopy; however small sample size because of solubility makes the results subject to high errors; because small differences in temperature correspond to large differences in molecular weights. Nevertheless, adequate results were obtained to indicate the degree of association of complexes in solution.

(a) $Pt(DPFPBA)_2$ M = 667

requires M = 809

(b) $[Pd(DPFPBA)_2]_2$ M = 730

n = 1 requires M = 720

n = 2 requires M = 1440.

4.8 N.M.R. Data

The ^{13}C n.m.r. data for the complexes is contained in Table 4.8; the notation used is described in Figure 4.3. Before discussing the data a number of points should be noted. All the complexes showed some decompositions. The platinum complexes suffered from small sample size and solubility problems which may account for the lack of C-1 (NCN) peaks in the spectrum.

Signals for the carbon atoms of substituent groups for the platinum compounds relate closely to those of the palladium and nickel compounds with the same ligand, for which C-1 peaks are found. The $Ni_2(DPFPBA)_4$ data should be considered with caution since it was apparent both optically and spectrally that considerable decompositions had occurred. In the $Ni_2(DPBA)_4$ case slight decomposition was noted also during spectrum acquisition.

The C-1 (NCN) signals found for both the nickel and palladium complexes occur *ca.* 175 p.p.m., a value similar to that found by Kilner[5] for chelate Re complexes (*ca.* 167 p.p.m.), which have a NCN delocalised system. The C-1 values were all around 22 p.p.m. downfield of those for the parent

TABLE 4.8 ^{13}C N.M.R. Data for Bis-Amidino Pt(II) and Pd(II) Complexes

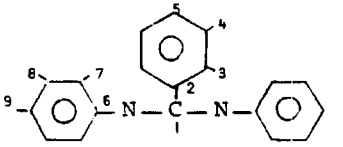


Figure 4.3

LIGAND	Metal	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-H	CH_3	T°C	SOLVENT	NOTES
DPAA	Pt						132.6	127.9	129.6	121.6		17.5	25	$(CD_3)_2O$	Peak at 1531 ppm. assigned to free ligand
DMBA	Pt	167.6	132.9	128.5	129.3	132.3						30.3	25	$CDCl_3$	No significant change at -80° except for a small amount of decomposition.
DPBA	Pt	-	135.0	128.2	129.2	127.0	143.4	123.0	128.5	122.2			25	$CDCl_3$	A peak observed at 154.1 ppm. was assigned to free ligand in the Pt case. Ni spectrum, see Table 4.11.
	Pd	-	132.0	128.3	129.1	126.1	144.1	124.7	129.0	122.7			25	$CDCl_3$	
	Ni	174.1	132.2	-	129.4	126.8	145.8	123.1	-	122.3			25	C_6D_6	
DPTBA	Pd	174.4	133.0	128.4	129.6	126.2	-	125.4	129.3	132.3		20.8	25	CD_2Cl_2	Low-temperature spectrum of Pd complex indicated a second species present in small amounts.
	Pd	176.2	132.0	128.0	128.8	126.5	144.1	124.6	128.5	131.6		20.2	-80	CD_2Cl_2	
	Pt	-	132.3	128.1	129.0	126.8	140.8	124.7	128.5	130.1		20.7	25	$CDCl_3$	
DPFPBA	Pd	176.2	131.2	128.4	129.2	130.1	140.7 (J_{C-F}=2)	126.0 (J_{C-F}=7)	115.1 (J_{C-F}=22)	159.3 (J_{C-F}=242)			40	CD_2Cl_2	Low-temperature spectrum of Pd complex indicated a second species present in small amounts.
	Pd	175.8	130.6	128.2	128.9	129.9	140.0	125.6 (J_{C-F}=7)	114.9 (J_{C-F}=22)	158.9 (J_{C-F}=242)			25	CD_2Cl_2	
	Pd	175.3	130.4	127.6	128.4	129.4	139.6	125.0 (J_{C-F}=7)	114.4 (J_{C-F}=22)	158.6 (J_{C-F}=242)			-80	CD_2Cl_2	
	Pt	-	130.1	128.5	128.9	129.5	139.1	126.0	114.9 (J_{C-F}=22)	159.0 (J_{C-F}=242)			25	$CDCl_3$	
	Ni	171.6	130.9	128.5	130.9	131.7	147.5	127.3	114.9 (J_{C-F}=23)	159.2 (J_{C-F}=243)			25	$CDCl_3$	
DPIPBA	Pt	-	132.0	128.0	129.0	129.4	143.3	124.7	125.8	140.8	33.3	23.9	25	$CDCl_3$	
	Pd	174.8	131.7	127.9	128.9	129.8	142.8	124.4	125.9	141.2	33.3	23.9	25	$CDCl_3$	

Values in p.p.m. relative to T.M.S. J values in Hz.

amidines (Chapter Three). The only platinum C-1 value observed, for $Pt(DMBA)_2$ (167 p.p.m.) is also indicative of an NCN delocalised system.

Comparing the aromatic ring carbon signals with those of the free ligands the changes are negligible in many cases. One exception of note is the C-7 *ortho*-carbon of the N-substituent rings which are moved downfield to a considerable extent (Table 4.9).

TABLE 4.9 Changes in C-7, C-2 Carbon Signal Position due to Complexation of Amidines

Complex	C-7 Δ p.p.m.	C-2 Δ p.p.m.
$Pt(DPIPBA)_2$	+ 3	- 4
$Pd_2(DPIPBA)_4$	+ 4	- 4
$Pt(DPTBA)_2$	+ 3	- 2
$Pd_2(DPTBA)_4$	+ 4	- 2
$Pt(DPBA)_2$	+ 4	0
$Pd_2(DPBA)_4$	+ 4	- 3
$Ni_2(DPBA)_4$	+ 2	- 3
$Pt(DPFPBA)_2$	+ 4	- 4
$Pd_2(DPFPBA)_4$	+ 4	- 4
$Ni_2(DPFPBA)_4$	+ 5	- 3
$Pt(DMBA)_2$	+ 8	+ 3

The effect shows the localisation of electrons in the aryl rings because of the electron withdrawing effect of the metal. The other significant movement occurs in the C-2 signal which moves upfield in all cases except $Pt(DPBA)_2$,

which remains similar, and $Pt(DMBA)_2$ which moves downfield by 3 p.p.m. The data is consistent with a high electron density on the C-1 and C-2 carbons.

The low temperature n.m.r. spectra of both $Pd_2(DPFPBA)_4$ (Table 4.10) and $Pd_2(DPTBA)_4$ indicated the presence of another species, albeit in small amount. Variable temperature ^{19}F n.m.r. spectra of $Pd_2(DPFPBA)_4$ (Figure 4.4), shows a single peak at 25°C, and three peaks at -40°C. In the room temperature n.m.r. spectrum of $Ni_2(DPBA)_4$ (Table 4.11) two species were also found to be present, in approximately similar amounts. These results will be discussed later.

4.9 X-ray Structure Data

The structure of one of the complexes $Pt\{PhNC(Ph)NPh\}_2$ has been determined by X-ray crystallography by Dr. R.O. Gould of Edinburgh University. The crystal was grown from chloroform over an eight week period.

Data: $a = 26.714(7)$, $b = 6.031(2)$, $c = 20.586)3$ Å

$\alpha = 90^\circ$, $\beta = 6.031(2)$, $\gamma = 90^\circ$

Cell Volume = 2967 Å $2 = 4$, $F(000) = 1456$

$C_{calc} = 1.651 g\ cm^{-3}$

Radiation MoK, $\lambda = 0.71069$ Å $\mu = 47.8\ cm^{-1}$ [50.1].

$R = 0.022$ based on 1459 independent data.

Crystal Dimensions 0.6 x 0.3 x 0.2 mm (needles).

Space Group I2/2 alt. setting C_2/c.

FIGURE 4.4

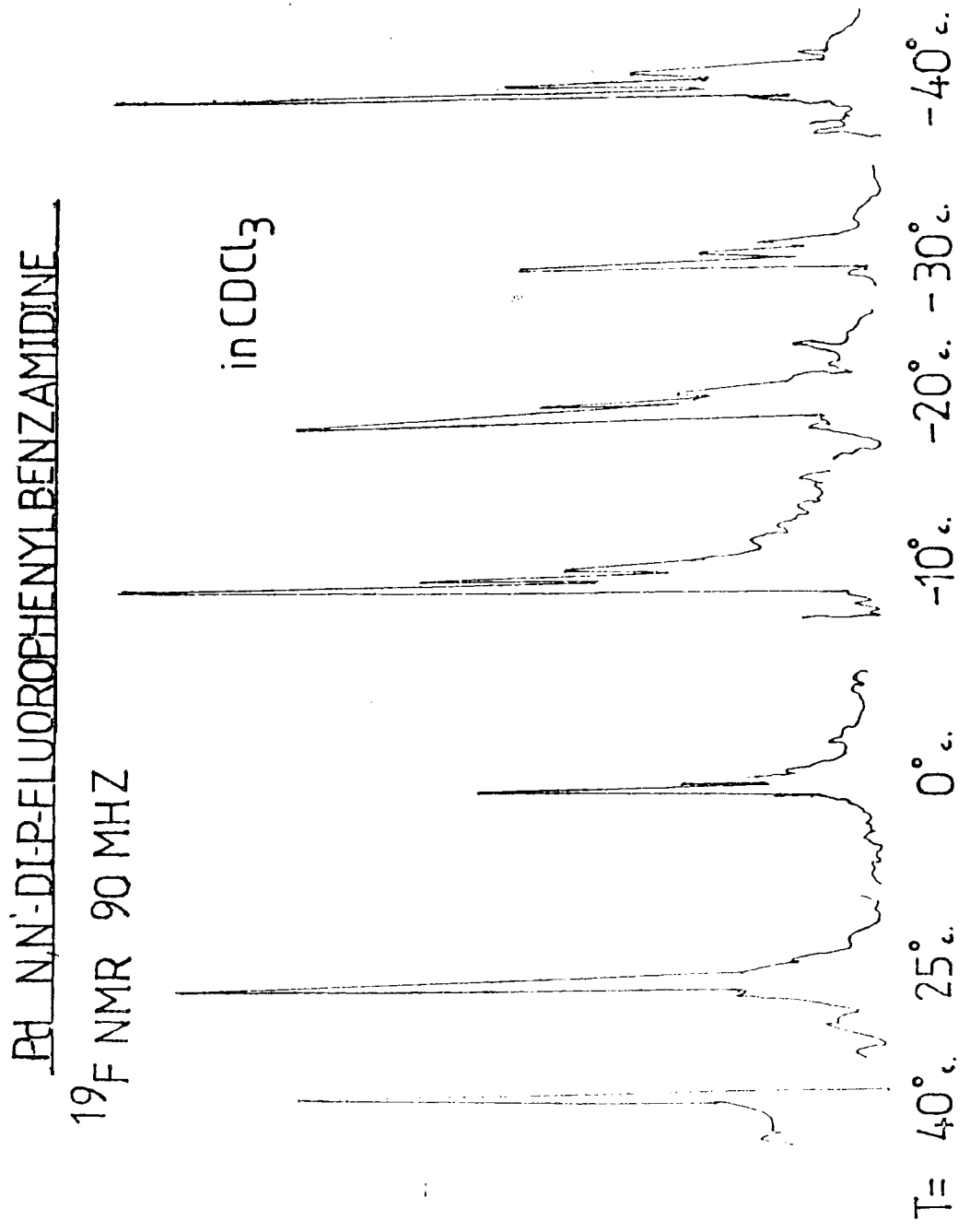

PH N,N'-DI-P-FLUOROPHENYLBENZAMIDINE
^{19}F NMR 90 MHZ
in $CDCl_3$
T= 40°c. 25°c. 0°c. -10°c. -20°c. -30°c. -40°c.

TABLE 4.10 The Variable Temperatures N.M.R. Data for $Pd_2(DPFPBA)_4$

MONOMER / DIMER	CARBON SIGNAL P.P.M.								
Temp. °C	C_1/C_1^1	C_2/C_2^1	C_3/C_3^1	C_4/C_4^1	C_5/C_5^1	C_6/C_6^1	C_7/C_7^1	C_8/C_8^1	C_9/C_9^1
+40	176.2	131.2	128.4	129.2	130.1	140.7 (J_{C-F}=2)	126.0 (J_{C-F}=7)	115.1 (J_{C-F}=22)	159.3* (J_{C-f}=242)
	-	-	-	-	-	-	-	-	-
+25	175.8	130.6	128.2	128.9	129.9	140.0	125.6 (J_{C-F}=7)	114.9 (J_{C-F}=22)	158.9 (J_{C-F}=242)
	-	-	-	-	-	-	-	114.3 (J_{C-F}=23)	158.2 (J_{C-F}=243)
-80	175.3	130.4	127.6	128.4	129.4	139.6	125.0 (J_{C-F}=7)	114.4 (J_{C-F}=22)	158.0 (J_{C-F}=242)
	165.4	130.1	127.7	128.6	129.4	139.7	124.6	113.7 (J_{C-F}=22)	157.5 (J_{C-F}=242)

*The C-H and non C-H signals were assigned using a DEPT experiment and their chemical shifts. Values in p.p.m. relative to T.M.S.. The "dimer" signals were of lower intensity than the "monomer" signals. On cooling to -80° some deposition was noted. J values in Hz.

TABLE 4.11 The ^{13}C N.M.R. Spectrum of $Ni_2(DPBA)_4$

CARBON SIGNALS								
C_1/C_1^1	C_2/C_2^1	C_3/C_3^1	C_4/C_4^1	C_5/C_5^1	C_6/C_6^1	C_7/C_7^1	C_8/C_8^1	C_9/C_9^1
174.1	132.2	-	129.4	126.8	145.8	123.1	-	122.3
173.1	131.5	-	129.3	-	145.0	123.0	-	121.5

Solvent C_6D_6 T = 25°C

- indicates peaks not observed because of solvent.

TABLE 4.12 ^{19}F Signals of DPFPBAH, $Pt(DPFPBA)_2$ and $Pd_2(DPFPBA)_4$ †

Ligand	$Pt(DPFPBA)_2$	$Pd_2(DPFBA)_4$	Temperature ^oC
122.3 ppm.	120.5 ppm.	120.1 ppm.	25, 40
	120.5 ppm.	120.1, 121.1, 121.8 ppm. (see Fig.4.3)	-40

† ref. = $CFCl_3$

The molecule has C_i symmetry and sits in the unit cell in such a way that the platinum atoms do not contribute to half the diffraction pattern. Hence the light atoms are much better defined than is normal in a structure containing platinum., and all the hydrogen atoms were located and refined. The structure was solved using the Patterson heavy-atom method, and refined using the DIRDIF method. All the non-hydrogen atoms were located in the first map. The hydrogen atoms were found in the difference map. The bond lengths, torsion angles, and bond angles for the molecule are listed in Tables 4.13 and 4.14, and 4.15.

4.10 The Reaction of Bis-amidino Complexes with Various Reagents

4.10.1 Reaction of $Pt(DPBA)_2$ with Carbon Disulphide

$Pt(DPBA)_2$ (0.0737g.; 0.1 mmol) was dissolved in carbon disulphide (5 mls.). After stirring for 30 hours no colour change or reaction occurred. The solution was heated to reflux for fourteen days; infra-red analysis indicated no reaction had taken place or adduct formation.

TABLE 4.13 Bond Lengths (A) not involving Hydrogen Atoms

Pt	-	N(1)	2.038 (12)	C(21)	-	C(22)	1.390(11)
Pt	-	C(2)	2.520 (15)	C(21)	-	C(26)	1.386(11)
Pt	-	N(3)	2.022 (12)	C(22)	-	C(23)	1.370(12)
N(1)	-	C(11)	1.406 (10)	C(23)	-	C(24)	1.382(12)
N(1)	-	C(2)	1.331 (10)	C(24)	-	C(25)	1.365(12)
C(11)	-	C(12)	1.375 (12)	C(25)	-	C(26)	1.383(12)
C(11)	-	C(16)	1.389 (11)	N(3)	-	C(31)	1.387(10)
C(12)	-	C(13)	1.372 (13)	C(31)	-	C(32)	1.380(11)
C(13)	-	C(14)	1.356 (14)	C(31)	-	C(36)	1.401(12)
C(14)	-	C(15)	1.358 (13)	C(32)	-	C(33)	1.384(13)
C(15)	-	C(16)	1.379 (12)	C(33)	-	C(34)	1.391(13)
C(2)	-	C(21)	1.497 (11)	C(34)	-	C(35)	1.370(13)
C(2)	-	N(3)	1.340 (10)	C(35)	-	C(36)	1.379(12)

TABLE 4.14 Bond Angles (degrees) for Bonds in Table 4.13

N (1)	- Pt	- C (2)	31.78(19)	C (2)	- C(21) - C(22)	121.2 (5)
N (1)	- Pt	- N (3)	63.71(19)	C (2)	- C(21) - C(26)	119.7 (5)
C (2)	- Pt	- N (3)	31.99(19)	C(22)	- C(21) - C(26)	119.1 (5)
Pt	- N (1)	- C(11)	134.70 (4)	C(21)	- C(22) - C(23)	120.3 (6)
Pt	- N (1)	- C (2)	94.5 (4)	C(22)	- C(23) - C(24)	120.4 (6)
C(11)	- N (1)	- C (2)	127.6 (5)	C(23)	- C(24) - C(25)	119.6 (6)
N (1)	- C(11)	- C(12)	120.0 (5)	C(24)	- C(25) - C(26)	120.7 (6)
N (1)	- C(11)	- C(16)	121.8 (5)	C(21)	- C(26) - C(25)	119.9 (6)
C(12)	- C(11)	- C(16)	118.2 (8)	Pt	- N (3) - C (2)	94.9 (4)
C(11)	- C(12)	- C(13)	120.9 (7)	Pt	- N (3) - C(31)	135.5 (4)
C(12)	- C(13)	- C(14)	120.8 (8)	C (2)	- N (3) - C(31)	129.3 (5)
C(13)	- C(14)	- C(15)	119.1 (8)	N (3)	- C(31) - C(32)	125.0 (5)
C(14)	- C(15)	- C(16)	121.4 (7)	N (3)	- C(31) - C(36)	116.8 (5)
C(11)	- C(16)	- C(15)	119.5 (6)	C(32)	- C(31) - C(36)	118.2 (6)
Pt	- C (2)	- N (1)	53.7 (3)	C(31)	- C(32) - C(33)	120.8 (6)
Pt	- C (2)	- C(21)	174.1 (4)	C(32)	- C(33) - C(34)	120.4 (7)
Pt	- C (2)	- N (3)	53.1 (3)	C(33)	- C(34) - C(35)	119.4 (7)
N (1)	- C (2)	- C(21)	126.8 (5)	C(34)	- C(35) - C(36)	120.4 (7)
N (1)	- C (2)	- N (3)	106.7 (5)	C(31)	- C(36) - C(35)	120.9 (6)
C(21)	- C (2)	- N (3)	126.3 (5)			

TABLE 4.15 Torsion Angles (degrees) for all Bonds

C (2) - Pt	- N (1) - C(11)	159.7	(7)
N (3) - Pt	- N (1) - C(11)	162.2	(6)
N (3) - Pt	- N (1) - C (2)	2.5	(3)
N (1) - Pt	- C (2) - C(21)	-97.5	(40)
N (1) - Pt	- C (2) - N (3)	175.8	(6)
N (3) - Pt	- C (2) - C(21)	86.7	(40)
N (1) - Pt	- N (3) - C (2)	-2.4	(3)
N (1) - Pt	- N (3) - C(31)	-177.1	(6)
C (2) - Pt	- N (3) - C(31)	-174.6	(7)
Pt - N (1)	- C(11) - C(12)	-42.1	(8)
Pt - N (1)	- C(11) - C(16)	133.2	(5)
C (2) - N (1)	- C(11) - C(12)	112.0	(7)
C (2) - N (1)	- C(11) - C(16)	-72.6	(8)
Pt - N (1)	- C (2) - C(21)	172.6	(5)
Pt - N (1)	- C (2) - N (3)	-3.5	(5)
C(11) - N (1)	- C (2) - Pt	-116.8	(6)
C(11) - N (1)	- C (2) - C(21)	10.7	(9)
C(11) - N (1)	- C (2) - N (3)	-165.4	(5)
N (1) - C(11)	- C(12) - C(13)	177.2	(6)
C(16) - C(11)	- C(12) - C(13)	1.7	(10)
N (1) - C(11)	- C(16) - C(15)	-177.8	(6)
C(12) - C(11)	- C(16) - C(15)	-2.3	(9)
C(11) - C(12)	- C(13) - C(14)	0.2	(12)
C(12) - C(13)	- C(14) - C(15)	-1.5	(12)
C(13) - C(14)	- C(15) - C(16)	0.7	(12)
C(14) - C(15)	- C(16) - C(11)	1.2	(11)
Pt - C (2)	- C(21) - C(22)	162.8	(37)
Pt - C (2)	- C(21) - C(26)	-17.8	(43)
N (1) - C (2)	- C(21) - C(22)	69.7	(8)
N (1) - C (2)	- C(21) - C(26)	-110.8	(7)
N (3) - C (2)	- C(21) - C(22)	-114.9	(7)
N (3) - C (2)	- C(21) - C(26)	64.5	(8)
Pt - C (2)	- N (3) - C(31)	175.2	(7)
N (1) - C (2)	- N (3) - Pt	3.5	(5)
N (1) - C (2)	- N (3) - C(31)	178.7	(5)
C(21) - C (2)	- N (3) - Pt	-172.6	(5)
C(21) - C (2)	- N (3) - C(31)	2.5	(10)
C (2) - C(21)	- C(22) - C(23)	177.7	(6)
C(26) - C(21)	- C(22) - C(23)	-1.7	(9)
C (2) - C(21)	- C(26) - C(25)	-178.3	(6)
C(22) - C(21)	- C(26) - C(25)	1.1	(9)
C(21) - C(22)	- C(23) - C(24)	2.0	(10)
C(22) - C(23)	- C(24) - C(25)	-1.7	(10)
C(23) - C(24)	- C(25) - C(26)	1.1	(10)
C(24) - C(25)	- C(26) - C(21)	-0.8	(10)
Pt - N (3)	- C(31) - C(32)	-152.1	(5)
Pt - N (3)	- C(31) - C(36)	26.5	(8)
C (2) - N (3)	- C(31) - C(32)	34.8	(9)
C (2) - N (3)	- C(31) - C(36)	-146.6	(6)
N (3) - C(31)	- C(32) - C(33)	179.8	(6)
C(36) - C(31)	- C(32) - C(33)	1.2	(10)
N (3) - C(31)	- C(36) - C(35)	-179.5	(6)
C(32) - C(31)	- C(36) - C(35)	-0.8	(10)
C(31) - C(32)	- C(33) - C(34)	-0.6	(11)
C(32) - C(33)	- C(34) - C(35)	-0.6	(12)
C(33) - C(34)	- C(35) - C(36)	1.1	(11)
C(34) - C(35)	- C(36) - C(31)	-0.4	(11)

4.10.2 Reaction of $Pt(DPFPBA)_2$ with Triphenyl phosphine

$Pt(DPFPBA)_2$ (0.101g.; 0.125 mmol) was dissolved in T.H.F. (60 mls.) and excess triphenylphosphine (0.131g.; 5 mmol) added. The mixture was refluxed for a total of six hours; i.r. and mass spectroscopy indicated no reaction had occurred.

4.10.3 Reaction of $Pt(DPBA)_2$ with Pressurised CO

A 10^{-4} M toluene solution of $Pt(DPBA)_2$ was placed in an autoclave and pressurised with CO at 240 atm. before heating to 100°C for 18 hours. The resultant dark brown solution was filtered and subjected to i.r. and gas-chromatography-(porapak Q column) mass spectroscopy investigations, but decomposition products only were detected. No amidino-platinum carbonyl complex was detected.

4.10.4 Reaction of $Pt(DPBA)_2$ with Synthesis Gas

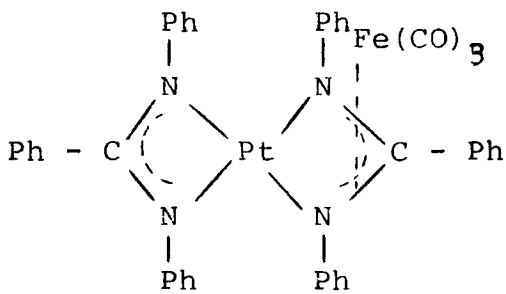
A 10^{-4}M solution in toluene (80 ml.) of $Pt(DPBA)_2$ was reacted with synthesis gas (CO,1:H_2, 2) at 160 atm. for 26 hours at 150°C. On completion of the reaction, the solution was grey in colour, and black metallic particles were noted. Clearly substantial decomposition had occurred. Analysis of the solution (g.c./m.s.) indicated a trace of compound having M^+ (m/e 108), which may be $PhCH_2OH$. Small quantities of light green solid were separated by evaporation of the solvent, but could not be identified (weak ions were noted in the mass spectrum - m/e 295, 281, 257, 211 and strong ions detected at m/e 167, 148, 119, 105, 77, 69 and 55).

4.10.5 Reaction of $Pt(DPTBA)_2$ with excess Sodium Metal

To $Pt(DPTBA)_2$ (0.159g.; 0.2 mmol) in T.H.F. (40 ml.) excess sodium (2.92g.; dried and washed with hexane) was added. The solution became dark black in colour after fifteen minutes, but no further colour changes occurred over 48 hours. The solution was filtered into a solution of PPNCl; (PPNCl = bis[triphenylphosphoranylidene]ammonium chloride); $[(C_6H_5)_3P_2]_2NCl$, (0.114g.; 2.5 mmol in dichloromethane (20 ml.)/T.H.F. (5 mol.) mix;) to yield a green-brown mixture. Black metallic particles, probably platinum were present in the residue. The liquor was reduced to the solid *in vacuo*, and then extracted with toluene (20 ml.). After filtration, addition of hexane to the liquor failed to precipitate any product, but removal of the solvents *in vacuo* yielded a dark-yellow solid. The solid was recrystallised from diethyl ether (50 ml.) to yield a very small quantity of brown product. The infra-red spectrum of the product indicated little except the presence of amidino ligand. Analysis by electron-impact mass spectroscopy was unsuccessful, only fragments of the PPN^+ ion being observed. The F.A.B. m/s (glycerol mull) proved more fruitful, but was dominated by the PPN^+ ion. Ion at m/e 538 (base peak) attributable to PPN^+, m/e 461 attributable to $[(Ph)_3P]^+$, and m/e 185 attributable to Ph_2P, were all of strong intensity. It was difficult to assign any of the other peaks observed in the spectrum except for m/e 195 attributable to ^{195}Pt and m/e 207 attributable to $[CH_3C_6H_4NCN\ C_6H_4]^+$. It was not possible on the basis of the data to identify the product.

4.10.6 The Reaction of $Pt(DPBA)_2$ with $Fe(CO)_5$

An attempt has been made to use the high electron density of the NCN fragment of the co-ordinated ligands in the bis-amidino for π-bonding to an iron carbonyl as in Figure 4.5.



(Figure 4.5)

A mixture of $Pt(DPBA)_2$, (0.184g.; 0.25 mmol) and $Fe(CO)_5$ (0.0979g.; 0.06 ml.; 0.5 mmol) in T.H.F. was irradiated by a mercury ultra-violet lamp for 4½ hours, yielding a green solution. Chromatography of the solution (alumina, Beckman gradel) yielded $Fe(CO)_5$ and an unidentified green product which was shown not to contain any Fe(Am) or Pt-Fe linkages by mass spectroscopy, and the infra-red spectrum of the green product showed no carbonyl bands. The reaction to produce the desired product did not occur in this case, however, there are a large number of other candidates which may take advantage of the NCN electron density, *e.g.* Pd(cyclooctadiene)$_2$ or $Pd(PhCN)_2Cl_2$, and future work may be more successful using these.

4.10.7 The Reaction of $Pt(DPBA)_2$ with 1-methyl-imidazoline-2-thione

This reaction resulted in the formation of a polymeric film and it is discussed fully in Appendix B.

4.11 Discussion

The nickel group complexes $[M(Am_2]_n$, n=1 or 2 are formed in reasonable yield by the reaction of $[M(PhCN)_2Cl_2]$ (M=Pt or Pd), or anhydrous $NiCl_2$ 0.3 $C_4H_{10}O_2$ with lithioamidines in ether solutions. The platinum complexes are monomeric according to mass spectroscopy, (Table 4.3), and cryoscopy, (Section 4.7), yellow solids, stable in air for short periods as solids, but are very air sensitive in solution. They are soluble in ethers, moderately soluble in chlorinated solvents, and slightly soluble in hydrocarbons. The palladium complexes are blood-red in colour except for $Pd_2(DMBA)_4$ which is yellow. They hydrolyse in air and decompose rapidly in solution in the presence of air. In chlorinated solvents over very long periods (weeks), under nitrogen, decomposition also occurs. The complexes are soluble in ethers and chlorinated solvents and moderately soluble in hydrocarbons. They are dimeric according to mass spectroscopy (Table 4.3) in the solid state but predominantly monomeric in solution. The nickel complexes are dark green solids which are unstable both as a solid and in solution, decomposition occurring even under nitrogen at room temperature. They are dimeric in the solid state according to mass spectroscopy (Table 4.3), and are soluble in most organic solvents. Decomposition occurs over several hours in chlorinated solvents. Attempts to purify the nickel group complexes by sublimation *in vacuo* resulted in decomposition. The complexes show a stability trend of Pt>Pd>Ni. A possible explanation of this lies in the increased value of the crystal field splitting 10 Dq,

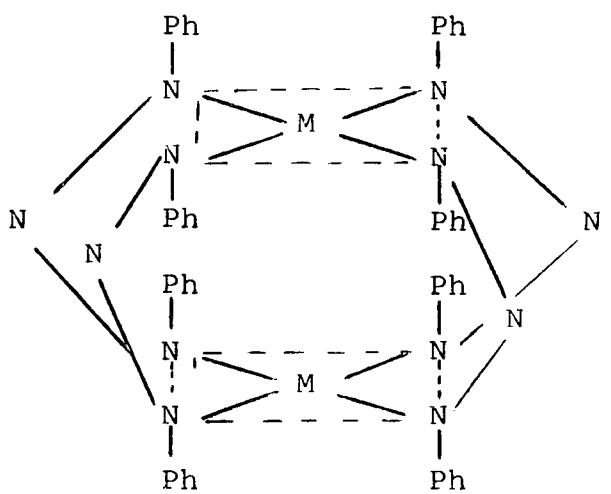
that accompanies the larger effective nuclear charge of the heavier atoms of the nickel system. Thus while Ni(II) complexes may be octahedral, tetrahedral or square-planar, those of Pt(II) and Pd(II) are almost exclusively square-planar. The stability of square-planar complexes relative to tetrahedral is very dependant on the stabilisation energy of the d^8 system. Ni(II) requires this stabilisation to be enhanced by the use of high field ligands, *e.g.* cyanides, whereas Pt(II) and Pd(II) require no special ligands to stabilise this mode of geometry. Thus, the instability of the Ni(II) complexes may be due to the amidino ligands being only partially successful in holding nickel (II) in a square-planar arrangement, attack above and/or below the plane by reactants being a facile process, which aids displacement of amidino groups.

A sixteen-electron rule applies in the case of these complexes because of the stabilisation of the d^8 square-planar configuration. The i.r. data previously mentioned (Section 4.6) for $M(Am)_2$ complexes is consistent with either a bridging or chelate mode of bonding, although the possibility of mono-dentate bonding cannot be entirely ruled out.

The ^{13}C n.m.r. data is consistent with a bidentate chelate mode of bonding in that the C-1 NCN signal (Figure 4.4) is observed in the majority of cases in the region in which the signal of the chelate groups in $Re(CO)_4$ Am[5], *c.a.* 175-166 p.p.m. have previously been observed, whereas for a dimeric briding amidine $[Ag_2(Am)_2]$[9] the C-1 signals have been observed in the 167-159 p.p.m. region. The substituent aryl and methyl groups at room temperature give rise to only one signal

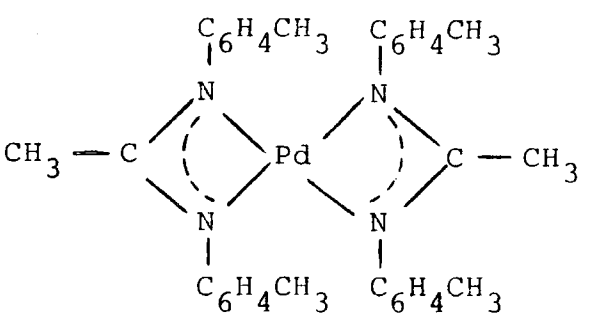
and hence indicate a symmetry about the N-C-N skeletal fragment consistent with a bidentate chelate or bridging mode of bonding. The ^{19}F n.m.r. data at room temperature is also consistent with either mode of bonding, a singlet being observed. Hence if we regard the amidines as bidentate ligands from this evidence they must be acting on 4-electron donors.

The mass spectral data (Section 4.3), indicates that the platinum complexes are monomeric, and both the palladium and nickel complexes dimeric in the solid state. It is postulated that the majority of the palladium complexes have similar structures to those determined for the related 1,3 diaryl triazene complexes[8] in the solid, *viz.*



(Fig. 4.6)

whereas the platinum complexes may be regarded as similar to $Pd[CH_3C_6H_4N\text{-}C(CH_3)NC_6H_4CH_3]_2$ which has also been crystallographically characterised[14] as,



(Fig. 4.7)

The nickel complex structures will be discussed later in the section.

One exception to the above statements is $Pt(DMBA)_2$ which yields a mass spectrum with a number of peaks at higher mass than the parent. The C-1(NCN) (Table 4.8), in the ^{13}C n.m.r. spectrum is also in the region which we shall later in the discussion assign to bridging groups. The i.r. spectra of both $Pt(DMBA)_2$ and $Pd_2(DMBA)_4$ are very similar, and it may be that the platinum complex is dimeric or exists as a monomer or dimer/oligomer mixture. It is not possible to decide either way on the basis of the data available.

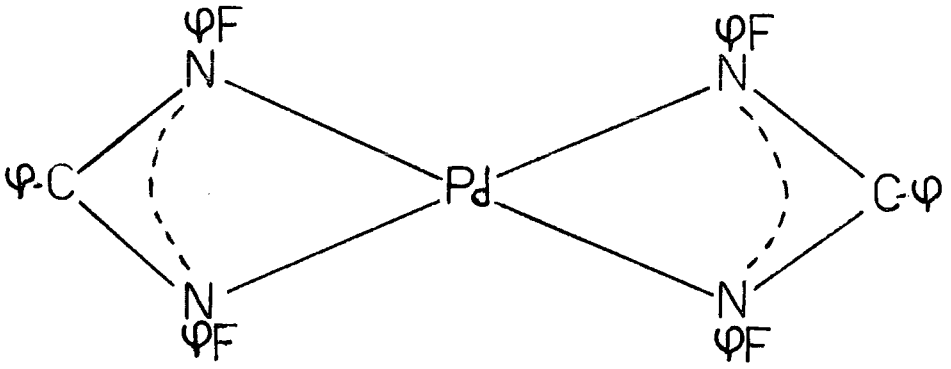
The ^{19}F n.m.r. of $Pt(DPFPBA)_2$ shows no fluxional behaviour with varying temperature, in contrast to $Pd_2(DPFBA)_4$, for which on cooling to -40^oC (Fig.4.4), the spectrum changes from a singlet to three signals. The ^{13}C n.m.r. at -80^oC also indicates the presence of more than one species (Table 4.10). There are several possible processes occurring in solution. The first involves [monomer] $\rightleftharpoons$ [dimer] $\rightleftharpoons$ [oligomer] equilibria. In freezing benzene solution the monomeric $Pd(DPFBA)_2$ (Section 4.7) predominates, and in the solid the dimer $Pd_2(DPFBA)_4$ is indicated by mass spectroscopy. It is possible that at room temperature in solution the monomer predominates and that as the solution is cooled the dimer starts to appear, and possibly oligomers also (Tables 4.8 and 4.10). Interestingly the C-1(NCN) signal for the new dimeric species *c.a.* 166 p.p.m. is very similar to that of $Pt(DMBA)_2$ which may also be dimeric, and both these C-1 signals are similar to those found by Vrieze[9] for silver formamidine dimers.

Interestingly Vrieze[9] has found a similar equilibria for amidines in solution concerning [dimer] $\rightleftharpoons$ [tetramer] equilibria for a number of silver and copper amidines. The ^{19}F data (Table 4.12) is, however, consistent with this postulate only if the concentrations of the individual species are also changing with temperature, as found by Vrieze.[9] The possible structures of the monomer, dimer and oligomer are described in Figure 4.8. The Nuclear Overhauser Effect requires that the intensities of the ^{13}C peaks be treated with caution; however, it is clear that even at -80°C the monomer is still much more predominant than the dimer, and of course any oligomers were not seen because of their small concentrations. Thus, the data for $Pd_2(DPFPBA)_4$ is consistent with a [monomer] $\rightleftharpoons$ [dimer] $\rightleftharpoons$ [oligomer] equilibria. The analogous nickel (1,3 diphenyltriazene) complex shows similar properties based on molecular weight measurements.[19] There is a significant change in the position of the C-1(NCN) signal from the postulated monomer to the postulated dimer, this may be attributable to the change in electronic environment when the monomeric chelate ligand has its skeletal C, NCN carbon moved out of the MN_4 plane to form a bridging dimeric species.

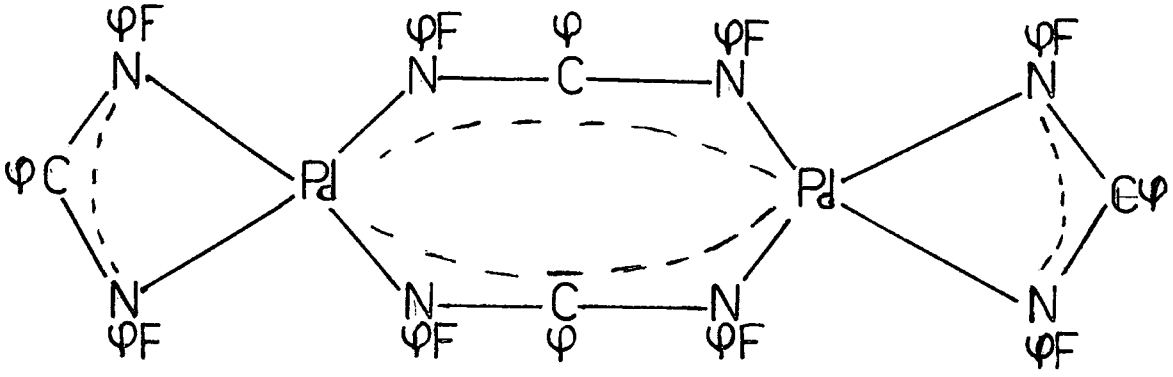
A second possibility is that of fluxionality of the amidino group which has been noted by a number of workers for amidines and related systems and is shown in Figure 4.9.

In Figure 4.9(a) breaking of a Pd-N bond occurs to give a tri-co-ordinated species, and Figure 4.9 b a di-co-ordinate species. The ^{19}F signals observed do not correspond to those theoretical possibilities given above, and knowing the well

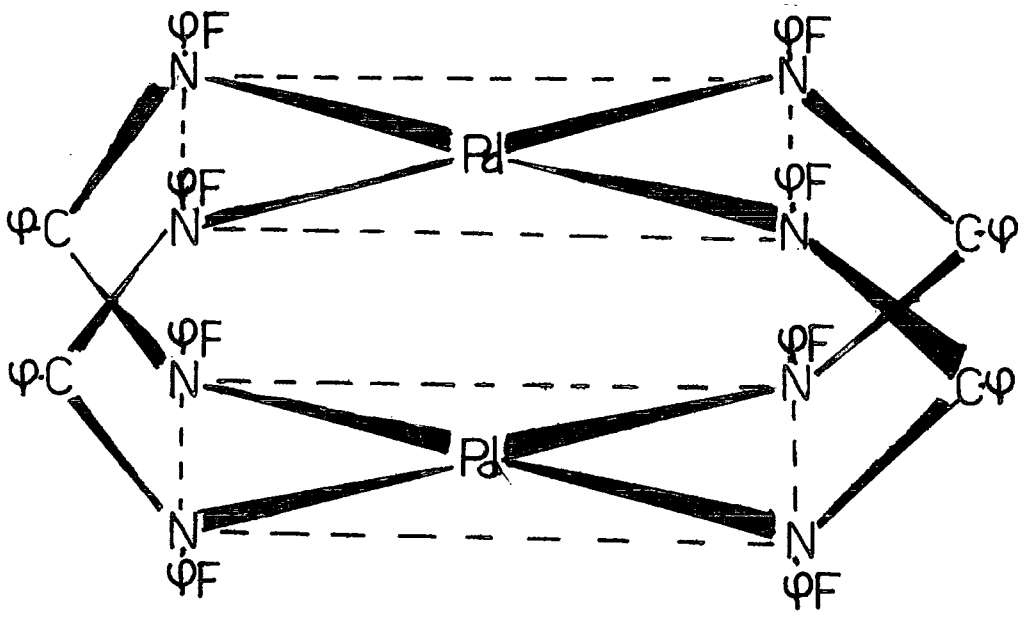
Figure 4.8 Possible Structures of $[Pd(DPFBA)_2]_n$ Monomers, Dimers and Oligomers.



Monomer

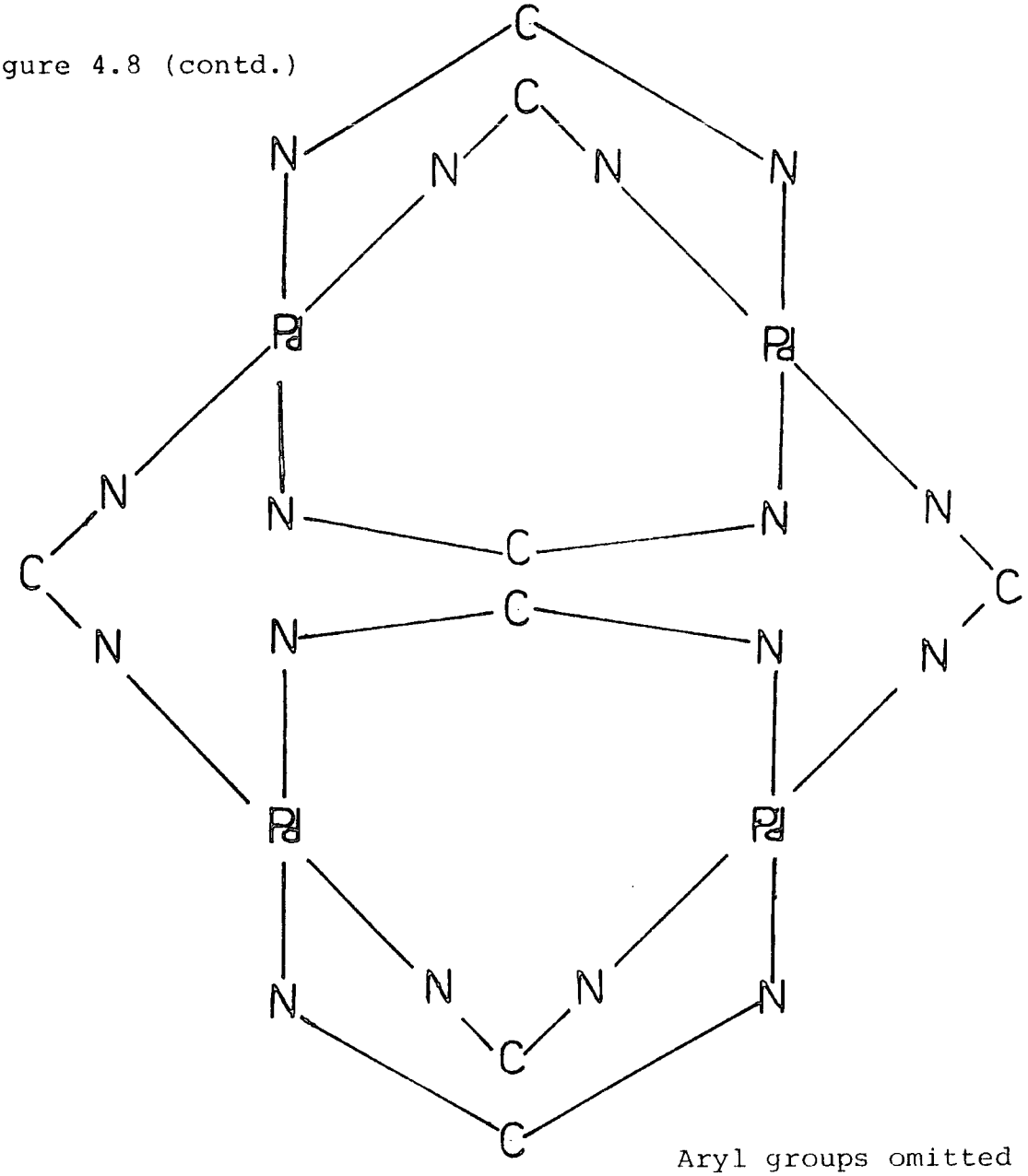


Dimer

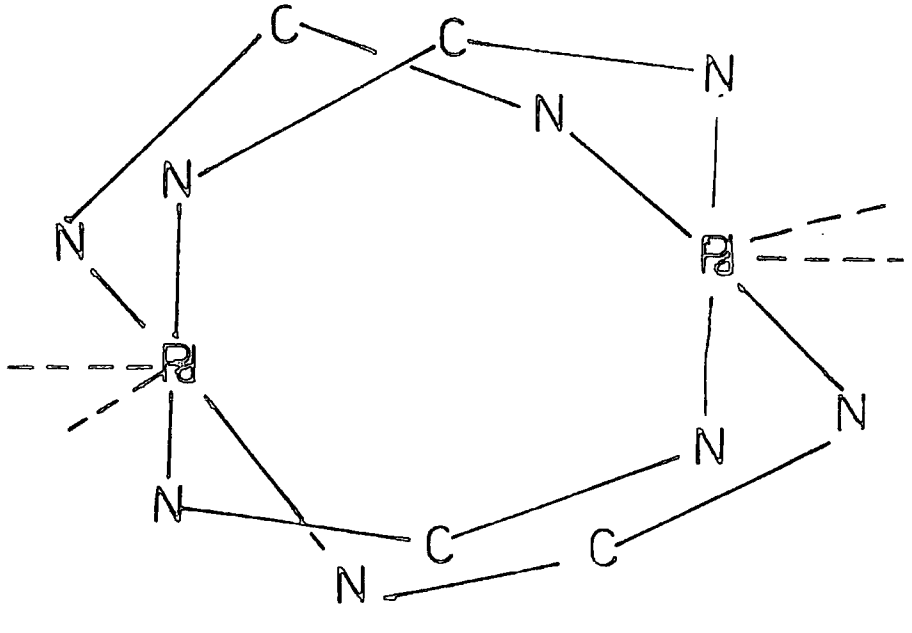


Dimer

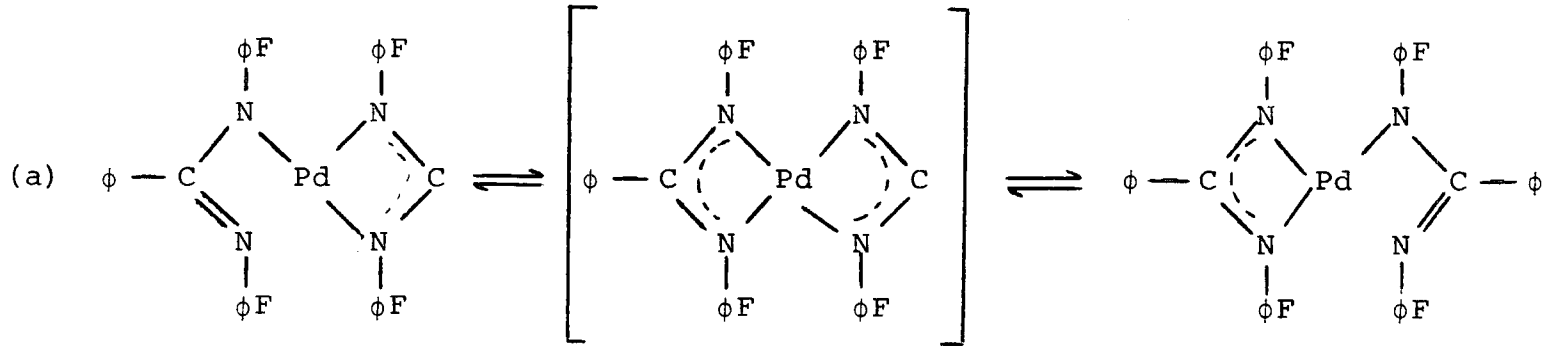
Figure 4.8 (contd.)



Aryl groups omitted
for clarity

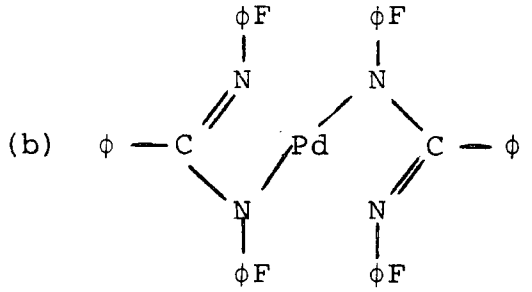


Oligomers



2 ^{19}F peaks 3:1 intensity, 1 ^{19}F peak intensity 4.

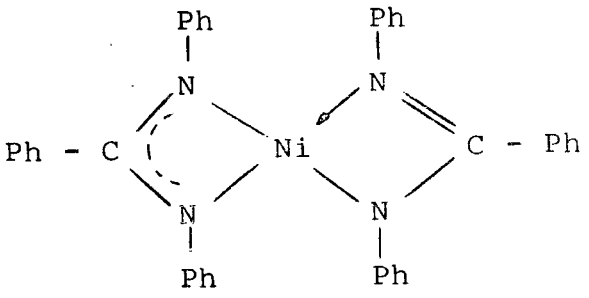
or both



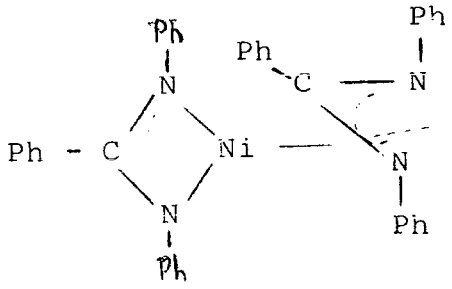
2 ^{19}F peaks intensity 2:2

Figure 4.9 Possible fluxional methanion for Pd-amidino Complexes.

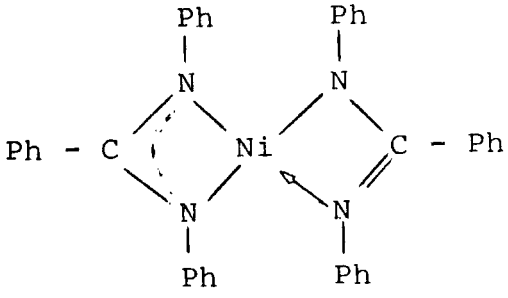
known preference for four-co-ordination in Pd(II) complexes, and that solvation effects may be discounted since all measurements were carried out in an ostensibly non-coordinating solvent. A fluxional process seems improbable. The n.m.r. and ancillary evidence (mass spectroscopy, cryoscopy) favour the explanation based on a [monomer] $\rightleftharpoons$ [dimer] equilibria in the $Pd_2(DPFPBA)_4$ case. The nickel case is more difficult to interpret because of the complexes labile nature. The ^{13}C n.m.r. spectra (Table 4.8) of $Ni_2(DPFPBA)_4$ is similar to those observed for $Pd_2(DPFPBA)_4$ and $Pt(DPFPBA)_2$ and is assigned to a monomeric species in a similar manner. $Ni_2(DPBA)_4$ in C_6D_6 has two sets of signals in the ^{13}C spectrum (Table 4.11). The small shift observed between the two C-1 signals, Δp.p.m. = 1, rules out the monomer-dimer equilibria which we have described for the palladium complexes. Solvation effects may be discounted since the spectrum was run in an ostensibly non-coordinating solvent. Clearly the slight differences in the values of the C-1 ^{13}C signals indicate that there are only very slight differences in the two skeletal C-1, NCN, carbon environments, and there are several possible structures which would fit this criteria, *e.g.* Figure 4.10. The monomeric complexes may be variations on any of the mixtures of bonding modes described . If we consider the structures, (Fig.4.10), I has been noted for a number of tantalum complexes[20] in the solid state, but since the bis(N,N´di-p-tolylacetamidino)palladium,[14] and bis(N,N´diphenylbenzamidino)platinum structures which have been determined by X-ray crystallography have two equivalent four-membered rings this possibility seems unlikely.



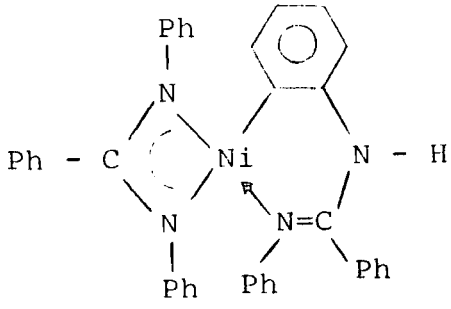
(I)



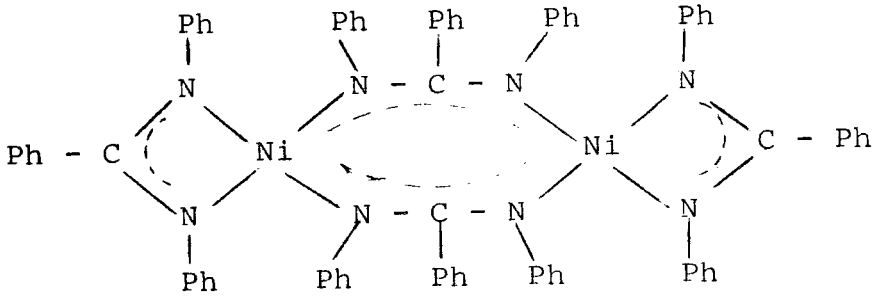
(II)



(III)



(IV)



(V)

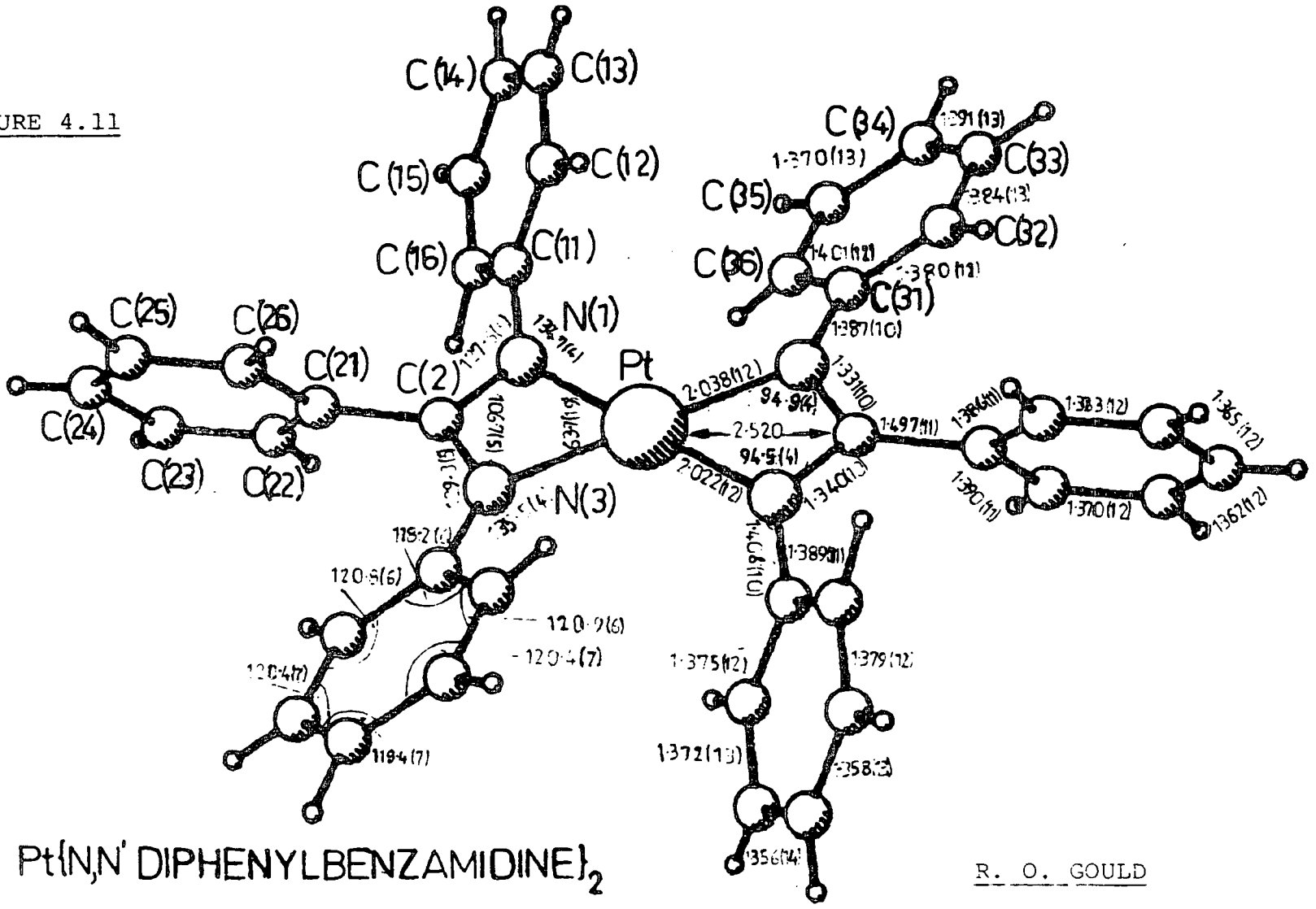
Figure 4.10 Possible Structures for $Ni(Am)_2$ Complexes

Structures II and III (Fig.4.10) would be unusual in amidine chemistry, and a monodentate/bidentate mixture of ligands would involve three-co-ordinate nickel again an improbable situation. The possibility of *O*-metallation IV (Fig.4.10) which has been noted for other metal, *i.e.* rhenium,[5] may be ruled out as there are no metal-carbon aryl ^{13}C signals in the spectrum which would be expected for an *O*-metallated complex. The dimer structure V (Fig.4.10) has all its skeletal C-1, NCN carbons in the same plane, and the square-planar arrangement around the nickel allows only subtle changes in the electronic environments of the C-1 carbons, and hence structure V (Fig.4.10) is a definite possibility for the structure of the nickel complex. Surprisingly the structure is not analogous to that of $Ni_2(PhNNNPh)_4$[8] which has been determined by X-ray crystallography, and resembles that of $Pd_2(PhNNNPh)_4$,[8] Figure 4.6.

It is clear that further work, n.m.r. and structural is required to fully understand the structural changes, and decomposition which these complexes undergo in solution.

The crystal structure of one of the complexes, $Pt\{PhNC(Ph)NPh\}_2$ has been determined using X-ray crystallography by Dr. R.O. Gould, University of Edinburgh. The structure is shown in Figure 4.11 and is very similar to that found for bis(N,N´di-p-tolylacetamidino)palladium(II) (Figure 4.12),[14] and for many aspects of structural significance the same conclusions apply to both complexes. The Pt-N distances in the complex (2.038Å and 2.022Å) are indicative of σ-N bonding and compare well with other M-N distances in which no π-interaction occurs (Table 4.16).

FIGURE 4.11



Pt{N,N' DIPHENYLBENZAMIDINE}$_2$

R. O. GOULD

FIGURE 4.12 Bis(N,N'di-p-tolylacetamidino)palladium(II)

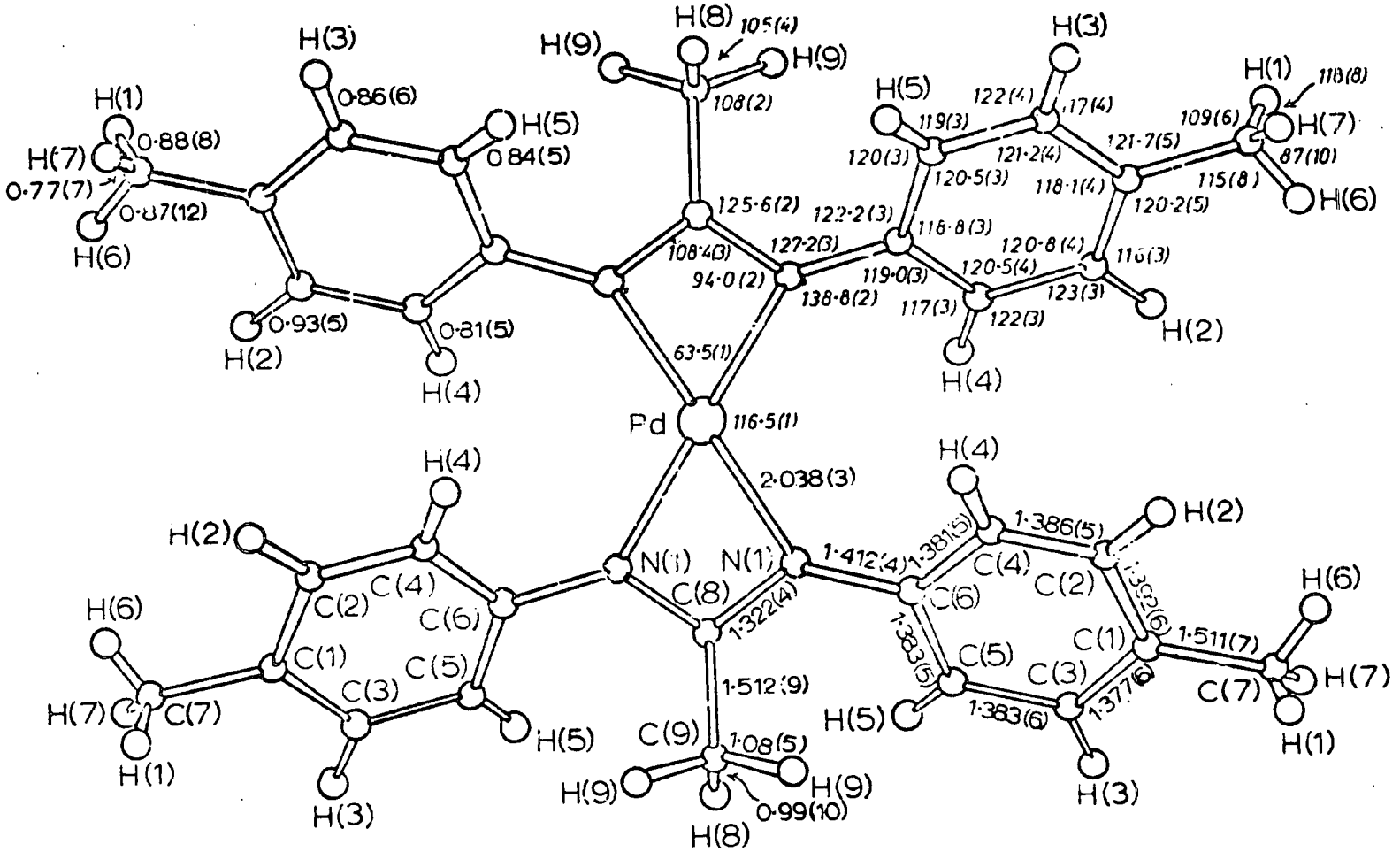


TABLE 4.16 M-N distances for a number of σ-N bonded complexes

Complex	M-N Å	Bonding Mode	Reference
bis(N,N´diphenylbenzamidino) platinum	2.038	bidentate	this work
bis (N,N´di-p-tolylacetamidino)palladium	2.038	bidentate	14
{2,6 bis[(dimethylamino) methylphenyl-CN,N´] (N^1N^2-di-p-tolylformamidine-N^1}platinum	2.132	monodentate	15
[(bis-acetamidine)chloride monohydrate]platinum	1.957	salt	16
[cis-chlorobis(triphenylphosphine)(1,3-di-p-tolyltriazenido)chloroform]palladium	2.11	monodentate	17
[trans-hydrido bis(triphenylphosphine)(1,3-di-p-tolyl triazenido)]platinum	2.09	monodentate	18
[dichlorobis(di-tertbutylcarbodiimide)]palladium	2.06	monodentate	21
[bis(triphenylphosphine)bis-(1,3-diphenyltriazenido)-benzene]platinum	2.089	monodentate	22
[(bis-triphenylphosphine)-chloro(1,3-di-p-tolyltriazenido)]palladium	2.033	monodentate	23

The C-N bond lengths (1.33 and 1.34Å) are intermediate between C-N (1.47Å) and C=N (1.27Å) covalent bond distances,[24] indicating a degree of delocalisation in the N-C-N skeletal system. A similar value was found for bis-(N,N´di-p-tolylacetamidino)Pd, (1.332Å).[14] The N-C phenyl bond lengths (1.387Å and 1.389Å) also indicate a certain degree of conjugation between the phenyl rings and the N-C-N system. The N_2C-C aryl bond (1.497Å) in the complex is intermediate between

the values for the C-C (1.54Å) and C=C (1.34Å) covalent distances,[24] indicating that delocalisation is present. Thus, the whole benzamidino system may be regarded as delocalised.

The important N-C-N "Bite", angle (106.25°) is of a similar order to that found for other bidentate amidino and related bidentate triazenido complexes (Table 4.17), but considerably smaller than N-$\hat{C}$-N for briding groups, *e.g.* Mo_2[diphenylbenzamidino]$_4$ N-$\hat{C}$-N = 117°. [28]

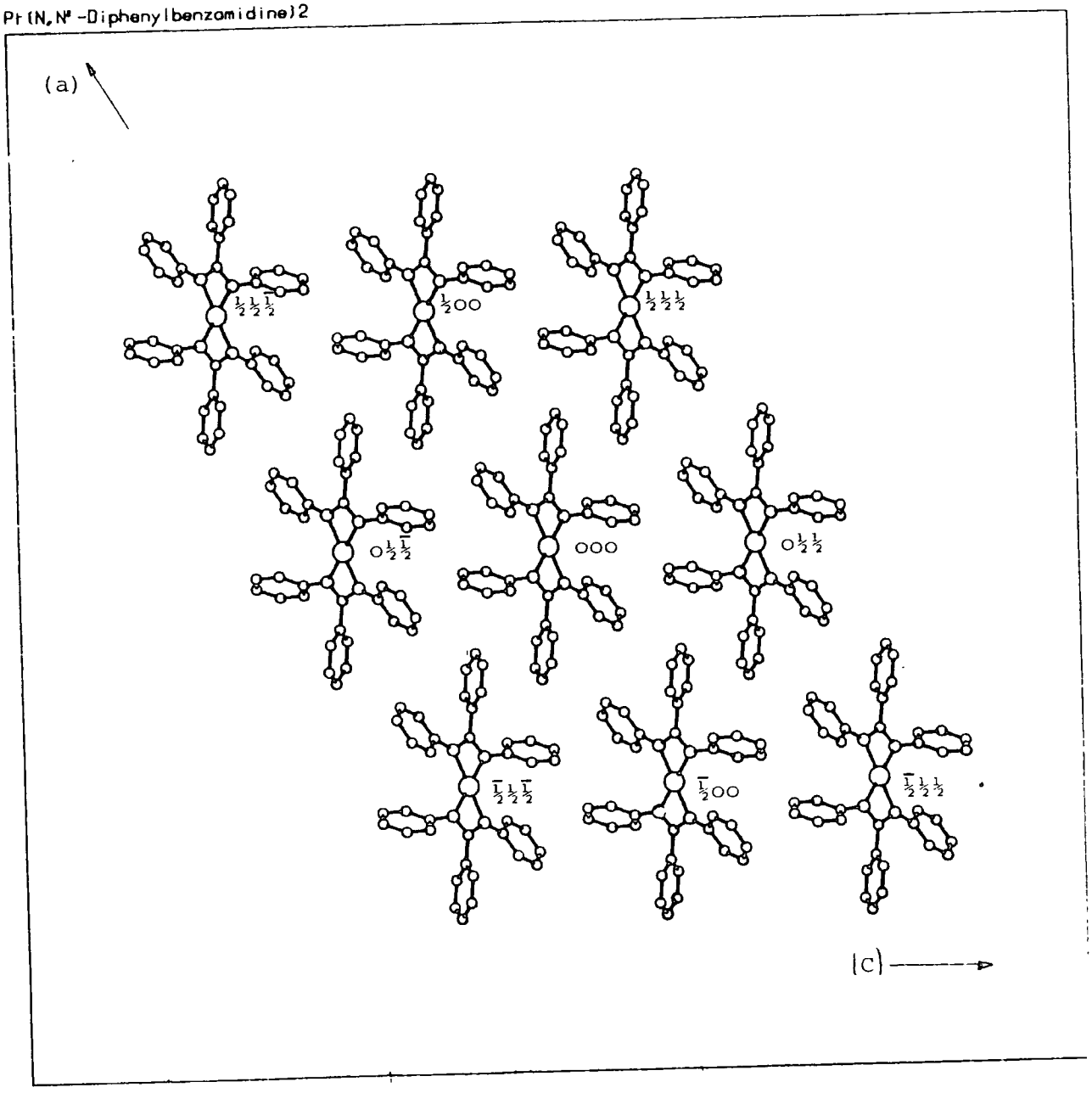
TABLE 4.17 N-$\hat{C}$-N and N-$\hat{N}$-N angles for Related Complexes

Complex	N-X-N†	Reference
bis(N,N´diphenylbenzamidino)platinum	106.25	this work
bis(N,N´di-p-tolylacetamidino)palladium	108.4	14
π-cyclopentadienyl dicarbonyl(N,N -di-phenylbenzamidino)molybdenum.	108.0	25
π-cyclopentadienyl dicarbonyl(1,3bis(3,5-bis(trifluoromethyl)phenyl)triazenido)-molybdenum	100.8	26
trans-bis(triphenylphosphine)carbonyl-(1,3di-p-tolyltriazenido)hydrido-ruthenium	105.2	27

† X = C for amidines, N for triazenes.

The crystal packing is shown in Figure 4.13 and shows the view along the b axis. The molecules are not directly stacked on top of each other and hence the smallest Pt-Pt 6Å indicates no metal-metal bonding which would be expected to

Packing diagram viewed along (b) showing relative placing



be of the order of that found in the metal 2.7746Å.[29] The smallest intra-molecular distances for the other atoms are given in Table 4.18.

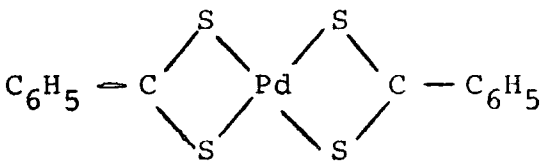
TABLE 4.18 Smallest Intramolecular Distances

Interaction	Actual Atom	Distance Å
C-C	$C_{12} - C_{30}$	3.370
C-H	$C_{23} - H_{34}$	2.880
C-N	$C_{36} - N_1$	3.662
H-H	$H_{16} - H_{26}$	2.447
H-N	$H_{16} - N_3$	2.881
N-N	$N_1 - N_3$	3.449

The C-C distances are of the same order as the layer distances in graphite 3.40Å.[30] Hence there appears to be no significant intramolecular interactions, and thus the geometry of the crystal is not significantly affected by the packing.

If we consider the structures adapted by related platinum and palladium complexes having groups isoelectronic with the amidino group, it is clear that the bonding modes of both the acetamidino and benzamidino groups differ markedly from that of carboxylato-, triazenido-, and allyl palladium, and platinum complexes. The acetate group adopts bridging positions in the polynuclear complexes $Pd_3(CH_3COO)_6$,[31] $Pd_2(\eta^3\text{-}C_3H_5)_2(CH_3COO)_2$,[32] $Pd_3(CH_3COO)_3(Me_2CNO)_3$,[33] and $[Pt_4(CH_3COO)_6(NO)_2 2CH_3COOH]$.[34] The triazenido complexes are either monodentate, cis $Pt(C_6H_5N\ NNC_6H_5)(PPh_3)_2C_6H_6$,[22] or bridging $Pd_2(C_6H_5NNNC_6H_5)_4$.[8] The allyl group adopts

the π-allyl bonding mode in Pd $(\eta^3 C_3H_5)(CH_3COO)_2$,[32] and a bridging mode in $[Pt(C_3H_5)Cl]_4$.[35] The amidino complexes do have an analogy in palladium and platinum chemistry however, in the four-membered chelate ring complexes of the dithiocarboxylate $(-C(=S)S-)$,[36] and dithiophosphate $(-P(=S)S-)$ ligands (Table 4.19). The structures of a number of these have been determined by X-ray crystallography, *e.g.* M(diethyldithiocarbamato)$_2$ (M=Pd or Pt),[48,49] and the structure of bis(dithiobenzoato)palladium(II), Figure 4.14, is directly analogous to the amidino platinum complex,



(Figure 4.14)

The molecule has a slightly larger "bite" S-L-S angle (112.6°) than the amidino-platinum complex and a similar $C_{skeletal}$-C phenyl bond distance of 1.47Å. The dithiophosphate complexes have been extensively studied by Stephenson[45,46,50-51] who found that $[M(S_2PPh_2)_2]$ (M=Pd or Pt) when treated with a tertiary phosphine underwent the following interesting reaction:[46]

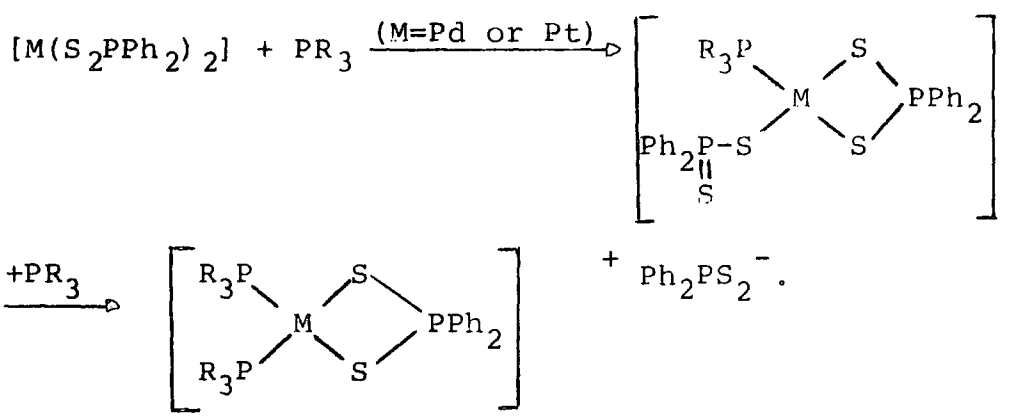
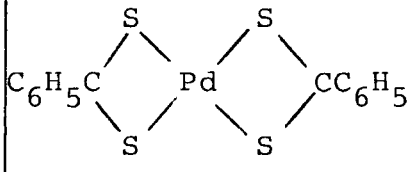
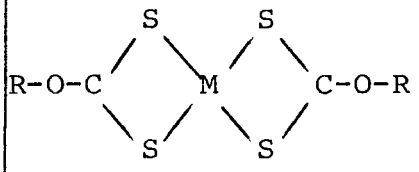
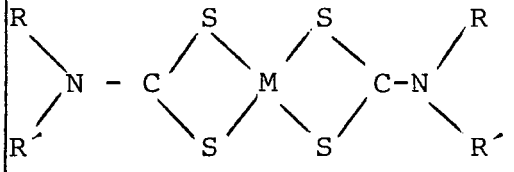
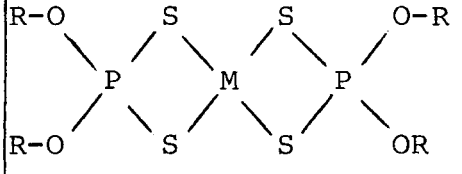
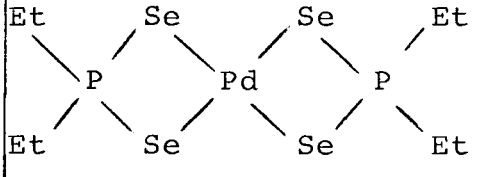


TABLE 4.19 Bidentate Sulphur Ligand Complexes Analogous to Bis-amidine Complexes

Complex	Ligand	Reference
	dithiobenzoate	41
	alkylxanthates	42-43
	dithiocarbamates	44
	dithiophosphate	45-46
	diselenophosphate	47

Note: M = Pd or Pt.

Attempts to achieve a similar reaction with $Pt(DPFPBA)_2$ were unsuccessful, as were reactions with CO, CS_2, and synthesis gas with platinum amidino complexes. The reaction of $Pt(DPBA)_2$ with 1-methyl-imidazoline-2-thione yielded an interesting polymer production reaction which is discussed in Appendix B.

Although not common, the σ, σ bidentate mode of bonding is known for the carboxylate-group in complexes of other metals, and it is fruitful to compare such data with that of the platinum and palladium amidino complexes. Bidentate acetate groups occur in $Zn(O_2CCH_3)_2(H_2O)_2$,[52] and although zinc(II) is slightly larger than palladium(II) a number of structural parameters are found to be similar, Table 4.20.

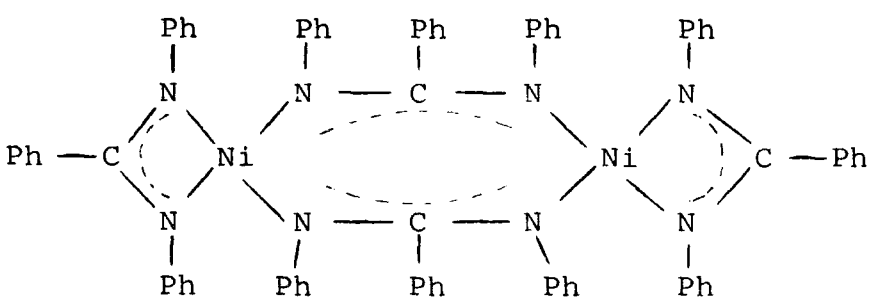
TABLE 4.20 Comparison of Crystallographic Data for symmetrically bound Acetato, Phosphinodithioato and Amidino Groups.

Parameter†	$Zn(O_2CCH_3)_2(H_2O)_2$	$Pt\{PhNC(Ph)-NPh\}_2$	$Pd\{p\text{-tolylNC-}(CH_3)N\text{-p-tolyl}\}_2$	$Pd(S_2PPh_2)_2(PPh_3)$
Z-X	1,30, 1.38	1.33, 1.34	1.33	1.99, Å
CH_3-X	1.48	-	1.52	- Å
M-X	2.18, 2.17	2.038,2.022	2.05	2.35,2.47 Å
X-X	2.21	2.14	2.17	3.14 Å
X-$\hat{Z}$-X	111	106.75	108.9	106 °
X-M-X	61	63.71	61.5	82 °
reference	(52)	(this work)	(14)	(51)

†X refers to the coordinating atoms, N in the amidine case, O in the carboxylate and S in the dithiophosphate, X-X refers to the non-bonding distance between coordinating groups. Z = C or P.

$Pd(S_2PPh_2)_2(PPh_3)$ is included to again make the point of the similarity of these ligands to each other. The "bite" angles for example are similar in all cases, as are the M-L bond lengths. Of particular note is the similarity of the structural parameters of the platinum and palladium complexes. Since two different amidine groups are used, and the same bonding mode adopted, a property of the metal may be the parameter determining factor. Both Pd(II) and Pt(II) have the same ionic radii (0.5Å)[24] and hence "ionic size". Thus "ionic size" and hence oxidation state because of their relation may determine the structural parameters of the ligand.

In contrast the palladium benzamidino complexes are thought to be analogous with the dimeric bridged (1,3-diphenyltriazene) complexes of nickel and palladium which have been characterised by X-ray crystallography.[8] The available evidence for the nickel complexes indicate that they have a dimeric structure of the type,



(Figure 4.15).

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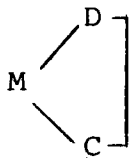
CHAPTER FIVE

O-METALLATED AMIDINE COMPLEXES OF PALLADIUM, PLATINUM AND NICKEL

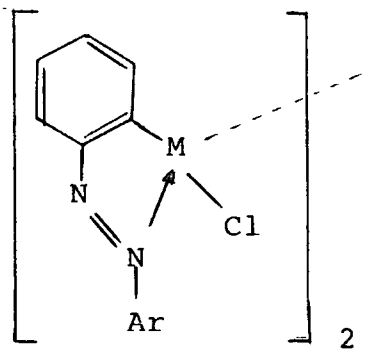
5.0 Introduction

The interest in cyclometallated complexes[1-3] is considerable because of the potential catalytic activity of such complexes. They are described as cyclometallated because they contain a ring system in which the metal is coordinated to a Group V (N,P,As) or Group VI (O,S) donor atom (D), as well as forming a M-C bond, *viz.*



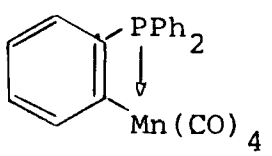
(Fig. 5.1)

A wide variety of such complexes are known, *e.g.*



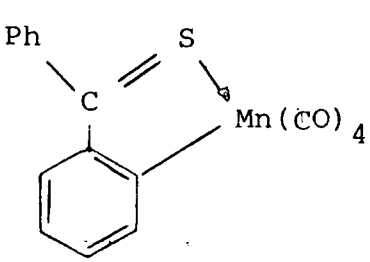
M = Pd or Pt. (4)

(Fig. 5.2)



(5)

(Fig. 5.3)



(6)

(Fig. 5.4)

There has been interest in *ortho*-metallated amidine complexes since Bradley[7] reported the first cyclometallated complex mercury N,N´-p-tolylformamidine. Here, as part of our investigation of the reactions of amidines with the nickel group metals, we have synthesised a number of related *O*-metallated derivatives of these metals.

NOMENCLATURE: Throughout this chapter, the preface (O-M) in the title of a complex denotes an *ortho*-metallated complex.

5.1 Experimental

(a) Palladium Complexes:

5.1.1 The reaction of K_2PdCl_4 with $p{\cdot}F{\cdot}C_6H_4NC(Ph)NC_6H_4{\cdot}F{\cdot}p$

DPFPBAH (0.3839g.; 1.25mmol), and K_2PdCl_4 (0.4080g.; 1.25mmol) were dissolved in 5:2 aqueous methanol (25 ml : 10ml) and the mixture refluxed for 2 hours. The resultant black/green solution was filtered whilst hot, yielding a dark-green solid product $[Pd(O\text{-}M\ AmH)Cl]_n$ as residue, and a yellow liquor. The product was washed with hexane (2x20 ml.), methanol (20 ml.) and finally hexane (20 ml.). The solvent was removed *in vacuo* to yield a yellow powder. Analogous reactions were achieved using DPTBAH, DPIPBAH, DPAAH, and DPFAH.

(b) Platinum Complexes:

5.1.2 The reaction of K_2PtCl_4 with PhNC(Ph)N(H)Ph

Preliminary investigations showed that if the synthetic route described in 5.1.1 was followed for the related

platinum complex decomposition occurred during the reflux stage to yield platinum metal. The following synthetic route was therefore used.

DPBAH (0.135g.; 0.5mmol), and K_2PtCl_4 (0.2075.; 0.5mmol) were dissolved in 2:5:3 methanol (20 ml.), water (50 ml.), diethyl ether (30 ml.) mixture. A very slight nitrogen bleed was used to remove very slowly the volatile solvent, and the reaction mixture was stirred vigorously at room temperature. After 2 hours the solution became orange in colour, and after 4 days a dark green-brown solid formed. On filtration a green-brown solid product $[Pt(O\text{-}M\ AmH)Cl]_n$ was isolated, which was washed with methanol (5 ml.) and then hexane (10 ml.). An analogous reaction was carried out with DPIPBAH.

(c) Nickel Complexes:

5.1.3 The Reaction of anhydrous $NiCl_2$ with $p\text{-}CH_3C_6H_4\text{-}NC(CH_3)N(H)C_6H_4CH_3p.$

Attempts to use the synthetic routes described in 5.1.1 and 5.1.2 resulted in no reaction. The following method was therefore used.

DPTAAH (4.76g.; 20mmol), and anhydrous $NiCl_2$ (2.592g.; 20mmol) were thoroughly mixed by grinding in a mortar. A Carius tube was then charged with the mixture. The tube was evacuated and the mixture heated at 200°C. for 24 hours. A dark brown insoluble solid resulted which was washed with diethyl ether (10x100 ml.), and then with warm diethyl ether (2x50 ml.). This resulted in the removal of unreacted organic material, but unreacted $NiCl_2$ remained in large amounts, and a pure complex could not be produced.

TABLE 5.1 Analytical Results

Complex	M.p.c. (dec.)	% Yield	Metal %	C %	N %	H %	Cl %
Pd(O-M) (DPFPBAH)Cl (green)	228	49.8	25.0 (23.69)	50.47 (50.82)	6.20 (6.24)	2.95 (2.90)	8.3 (7.90)
Pd(O-M) (DPBAH)Cl (green)	218d	66.8	26.3 (25.76)	55.35 (55.25)	7.01 (6.78)	4.16 (3.82)	9.88 (8.58)
Pd(O-M) (DPTBAH)Cl (green)	238	52.0	26.0 (24.12)	57.68 (57.18)	6.68 (6.35)	4.25 (4.31)	8.55 (8.04)
Pd(O-M) (DPIPBAH)Cl (green)	198d	27.9	20.0 (21.40)	58.82 (60.40)	5.61 (5.63)	5.83 (5.43)	7.05 (7.13)
Pd(O-M) (DPAAH)Cl (green-yellow)	252	45.8	30.00 (30.31)	47.85 (47.90)	8.10 (7.98)	4.01 (3.69)	9.76 (10.10)
Pd(O-M) (DPFAH)Cl (green)	232d	14.5	31.8 (31.57)	45.84 (46.33)	8.26 (8.30)	3.29 (3.26)	11.15 (10.51)
Pt(O-M) (DPBAH)Cl (green-brown)	208	15.6	35.9 (38.88)	46.50 (45.48)	5.36 (5.58)	3.81 (2.98)	6.85 (7.06)
Pt(O-M) (DPIPBAH)Cl (green-brown)	189	68.2	28.0 (33.30)	51.65 (51.25)	5.29 (4.78)	4.06 (4.77)	5.66 (6.04)

Found (calculated)

5.2 Infra-red Data

TABLE 5.2 Comparison of I.R. Vibrations of *Ortho*-metallated Complexes and Parent Amidines

AMIDINE USED	Metal	Highest frequency ν. (N-C-N) cm^{-1} complex	ν(N-C-N) asym. cm^{-1} parent amidine	ν(N-H) complex cm^{-1}
DPFPBAH	Pd	1606	1624	3300
DPBAH	Pd	1605	1630	3300
	Pt	1605		3290
DPTBAH	Pd	1605	1620	3300
DPIPBAH	Pd	1610	1620	3300 (3360a,3360b)
	Pt	1610		3290
DPAAH	Pd	1610	1624	3320
	Pt	1605		3480*
DPTAAH	Ni	1630	1630	3300*
DPFAH	Pd	1630	1670	3280 (3240c)
	Ni	1670		3300*

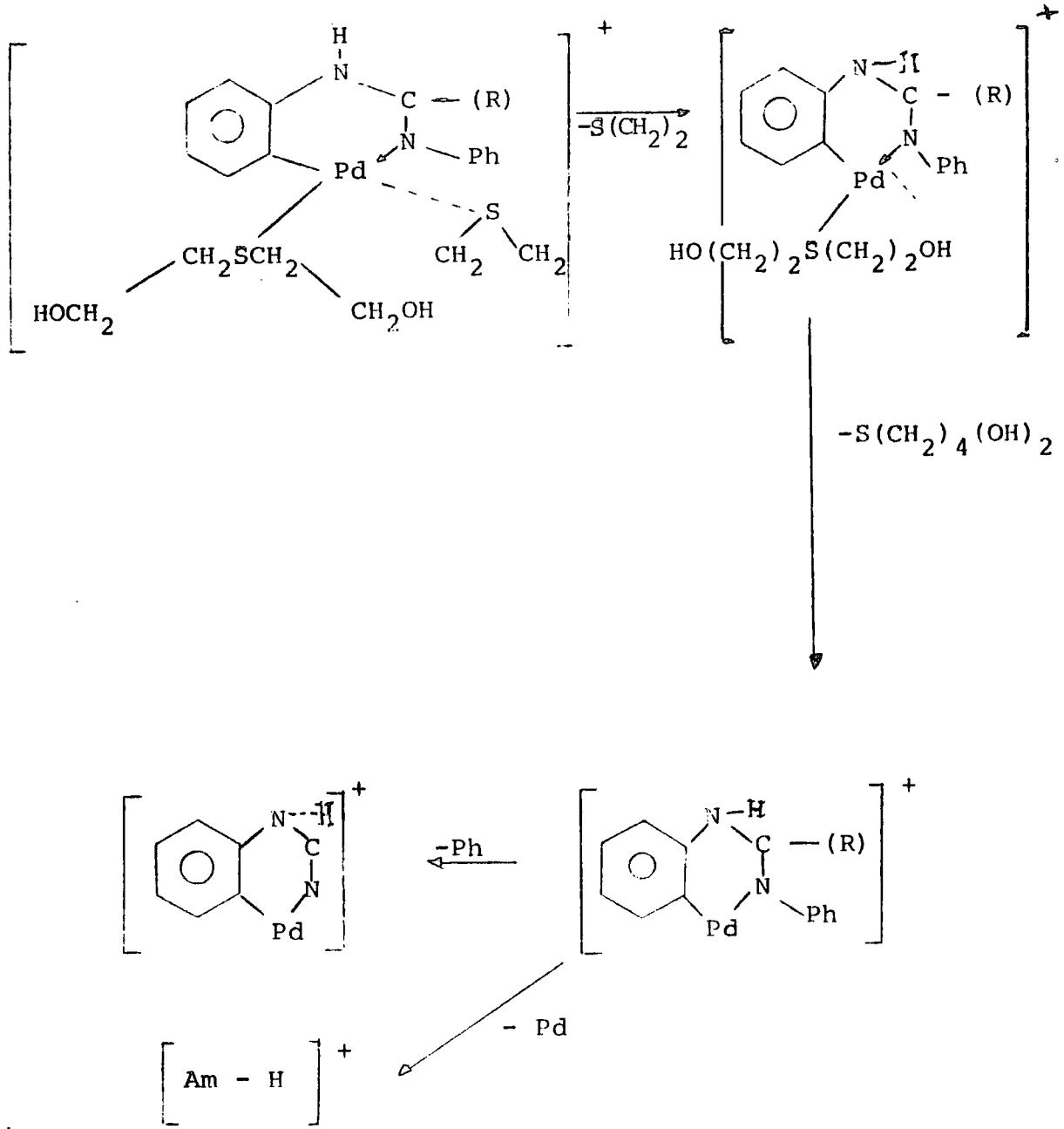
(a) recrystallised from D.M.S.O., (b) recrystallised from pyridine. All spectra were recorded nujol/hexachlorobutadiene mulls, using CsI/KBr plates.

* Not analytically pure.

5.3 Mass Spectra

The positive and negative ion electron impact and C.I. mass spectra of these complexes show only peaks associated with the ligand. The complexes were therefore analysed using positive ion F.A.B. mass spectrometry.

Figure 5.5 Mass Spectral Fragmentation Pathway for 6-membered ring complexes



Protonation / deprotonation is not an unusual process in F.A.B. m/s.

TABLE 5.3 Pd(O-M DPAAH) and Pd(O-M DPFAH) Mass Spectrum Assignmer

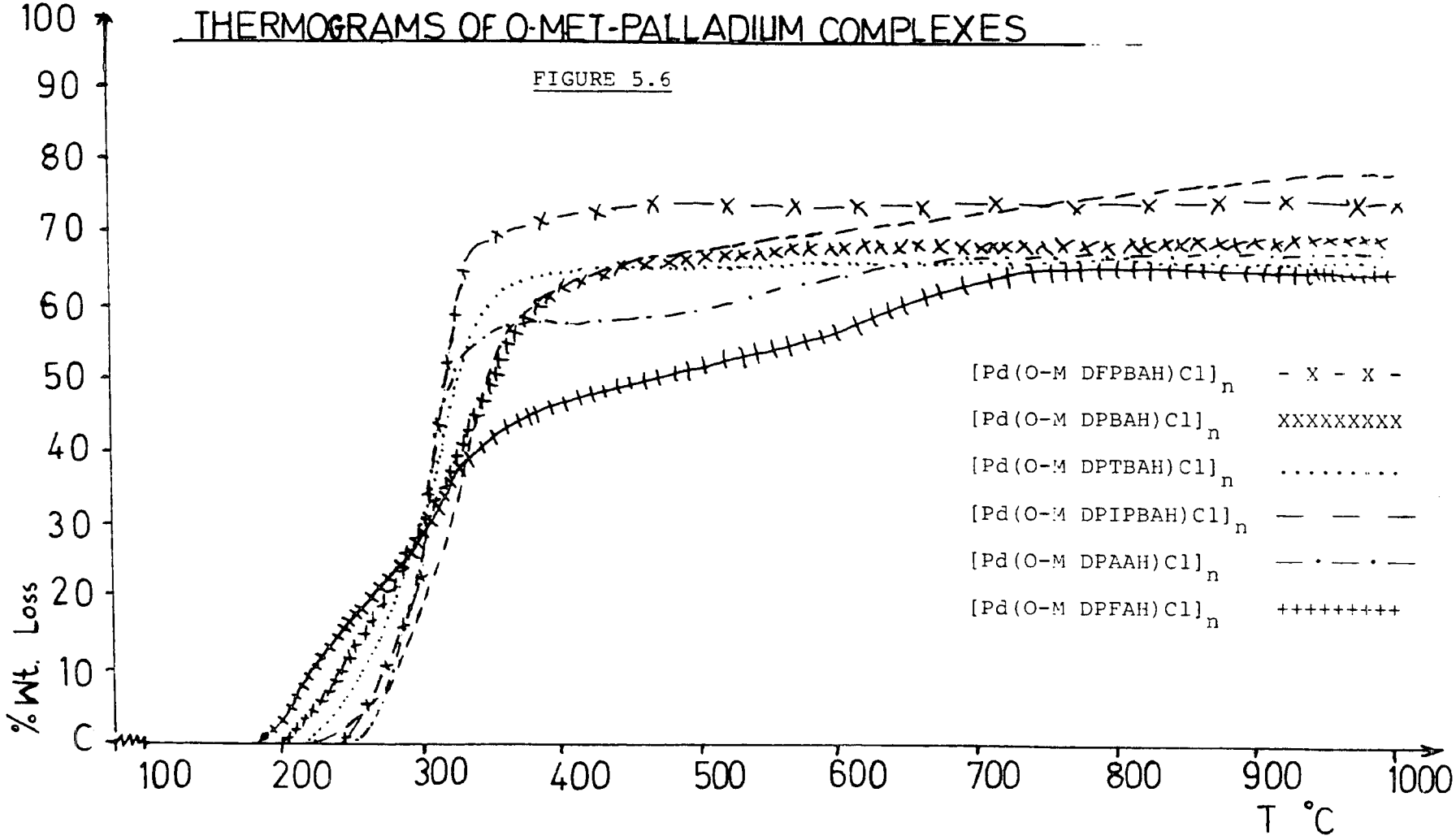
Ion Assignment†	Mass (% Ion Intensity)	
	Pd(DPFAH) Cl; R=H	Pd(DPAAH) Cl; R=CH_3
$[PhCN]^+ + H^+$	104 (25)	-
$[Ph(NNH]^+$	-	118 (39)
$[PhNC(R)NC_6H_4]^+$	195 (63)	209 (100)
$[PhNC(R)NC_6H_4]^+ + H^+$	198 (13)	210 (19)
$[PhNC(R)NC_6H_4]^+ + 2H^+$	197 (100)	211 (59)
$[PhNCNPd]^+ + H^+$	223 (0.7)	223 (4)
$[Pd(Am-H)]^+$	301 (5)	315 (6)
$[Pd(Am-H)DTG]^+$	423 (24)	437 (35)
$[Pd(Am-H)DTG.CH_2-S-CH_2]^+$	483 (2)	497 (3)

† Ions were verified by computer similation of isotope patterns. DTG; THIODIGLYCOL.

The two compounds were mulled in thiodiglycol and their fragmentation pathways are described in Figure 5.1. F.A.B. spectra of $[Pd(O\text{-}M\ DPTBAH)Cl]_n$ $[Pd(O\text{-}M\ DPIPBAH)Cl]_n$ $[Pd(O\text{-}M\ DPFPBAH)Cl]_n$ $[Pd(O\text{-}M\ DPBAH)Cl]_n$, $[Pd(O\text{-}M\ DPBAH)]_n$, $[Pt(O\text{-}M\ DPIPBAH)Cl]_n$ were run as glycerol mulls and proved less successful; the main peaks observed being attributable to $[Am-H]^+$. Traces of $[M(Am-H)_2]^+$ (M=Pt,Pd] were also present suggesting traces of the impurity $[M(Am-H)_2Cl_2]$.

5.4 Thermogravimetric Studies

The thermograms (Figure 5.6) are featureless, the residue being palladium metal corresponding to the theoretical palladium content of the complexes. The one distinct transition in


THERMOGRAMS OF O-MET-PALLADIUM COMPLEXES
FIGURE 5.6
% Wt. Loss
T °C
100
90
80
70
60
50
40
30
20
10
C
100
200
300
400
500
600
700
800
900
1000
[Pd(O-M DFPBAH)Cl]n - X - X -
[Pd(O-M DPBAH)Cl]n XXXXXXXXX
[Pd(O-M DPTBAH)Cl]n .....
[Pd(O-M DPIPBAH)Cl]n — — —
[Pd(O-M DPAAH)Cl]n — · — · —
[Pd(O-M DPFAH)Cl]n +++++++++

the complexes approximates to loss of amidine leaving residual [PdCl].

% wt. loss. (Found) Temp.range ^{o}C: Pd(DPIPBAH)Cl 70 (72) [0-439^{o}]; Pd(DPTBAH)Cl 68(68) [0-400^{o}]; Pd(DPBAH)Cl 66(65) [0-410^{o}]; Pd(DPFPBAH)Cl 39(72) [0-321^{o}]; Pd(DPFAH)Cl 58(44) [0-331^{o}]; Pd(DPAAH)Cl 60(61) [0-321^{o}].

5.5 E.S.C.A. Data

The low solubility of the complexes prevented the application of normal solvent based analytical techniques. Consequently an attempt was made to obtain E.S.C.A data (S.A.Johnson, University of Durham) on these complexes for characterisation purposes. Sample charging was determined by referring to the intense C_{1s} peak at a binding energy of 285.0eV.[8] The binding energy of the Pd $3d^5/2$ core level for the complexes was consistently 338.2eV, and since palladium is one of the elements for which a fairly good correlation between binding energy and oxidation state exists,[9] the element here can be assigned on oxidation state of +2. For comparison, binding energies [Pd/$3d^5/2$] of ∿335.7,[10] ∿336.0 (this work) 337.5-339.2[10] and 340.3eV[10] were found for the free metal, $Pd(PPh_3)_4$, a range of compounds involving the +2 oxidation state, and K_2PdCl_4 respectively. The Cl2$p^3/2$ core level binding energy of ∿198.1eV suggests its attachment to a metal,[11] but it is not possible to assign the chlorine to a terminal or bridging position. The C_{1s} spectrum is very intense because of the aryl rings, and the presence of unsaturation in these systems was confirmed by the C_{1s} shake-up satellite with

a kinetic energy some 6.6eV lower than the main photoionisation peak.[12] The N_{1s} signal exhibits a binding energy of ∿400.5eV which is fairly typical for nitrogen in an organic compound; however because of the low peak intensity, and the high intensity of the C_{1s} signals it was not possible to make a conclusion about the environments of the nitrogens.

5.6 N.M.R.

^{1}H and ^{13}C data are recorded in Tables 5.4 and 5.5.

5.7 Discussion

The reaction of amidines with K_2MCl_4 (M=Pd or Pt) in 5:2 refluxing aqueous methanol, or aqueous methanol/ether respectively results in the formation of complexes of the type $[M(O\text{-}M\ AmH)Cl]_n$. The formulation is based on elemental analysis, thermogravimetric analysis, mass spectroscopy and infra-red data.

The grey-green complexes formed were very insoluble involatile solids stable in air, but which decomposed slowly in solution yielding palladium/platinum metal. The insoluble and involatile nature of the complexes led to problems of characterisation, especially in n.m.r. where extremely long acquisition times were required to produce reasonable spectra.

The infra-red spectra of the complexes show a characteristic ν(N-H) vibration, *c.a.* 3300 cm^{-1}, a higher frequency than that associated with uncoordinated amidines (3230 cm^{-1}),

TABLE 5.4 ^{1}H N.M.R. of *o*-metallated palladium and platinum amidines (δ values)

Complex	N-H	C aryl	C other	Solvent
Pd(O-MDPFAH)Cl	10.1 (br)	7.81-[M-CH](d),7.80-7.29(8H)[aryl](m)	C-H 8.01 (1H) (s)	d^6 Acetone
Pd(O-MDPAAH)Cl	10.17(br)	7.78[M-CH](d), 7.34-7.22(3H)[o-met.ring H](m), 7.07-6.68(5)[aryl ring](m)	$C-H_3$ 1.97 (3H) (s)	d^6 DMSO
Pd(O-MDPIPBAH)Cl	n.o.	7.43(1H)[M-CH](d), 7.4-6.47(12H)[aryl rings](M)	C-H 2.78-2.56(2H)(m) CH_3 1.05(d) and 0.95(d)	d^6 Acetone
Pd(O-MDPTBAH)Cl	9.14	6.43-5.32(12H)[aryl rings](m)	CH_3 1.05(s) and 1.02(s) (br)	d^6 DMSO
Pd(O-MDPFPBAH)Cl	9.14	6.69-5.68(12H)[aryl rings](m)		d^6 DMSO
Pd(O-MDPBAH)Cl	9.15	6.65-5.71 [aryl rings](m)		d^6 DMSO
Pt(O-MDPBAH)Cl	9.43	7.39-6.42 [aryl rings](m)		$CDCl_3$
Pt(O-MDPIPBAH)Cl	9.36	7.19-6.22(12H)[aryl rings](m)	C-H 2.63(m) and 2.80(m). CH_3 CH_3 1.16 (d) and 1.01 (d)	$CDCl_3$

Key: d = doublet, m = multiplet, s = singlet, br = broad.
δ values relative to T.M.S., n.o.= not observed.

TABLE 5.5 ^{13}C N.M.R. of *O*-METALLATED COMPLEXES

COMPLEX	C1	C2	C3	C4	C5	C6	C7	C8	C9/C9	C10/C10	C11	Other	Solvent
Pd(O-MDPAAH)Cl	156.2	138.7	151.2	124.8	103.4	127.8	128.8	143.8	131.7	130.6	118.5	CH_3 23.25	d^6 DMSO
Pd(O-MDPFAH)Cl				129.9	124.7	130.5			119.9	129.5	124.5		d^6 Acetone

Key: all values in p.p.m. relative to TMS=0

COMPLEX	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15/C15	C16/C16	C17	Ca	Cb	Solvent
Pd(O-MDPIPBAH)Cl	163.5	138.2	142.5	128.8	129.4	128.3	127.5	146.3	126.9	124.7	131.3	125.3	127.2	146.0	126.7	125.4	131.7	CH 34.7 34.5	CH_2 24.7 24.4	d^6 Acetone
Pd(O-MDPTBAH)Cl			142.3												132.8	132.8		24.3		d^6 DMSO
Pd(O-MDFPBAH)Cl		132.1							119.1					133.0		118.0		-	-	d^6 DMSO
Pd(O-MDPBAH)Cl		132.2													119.4	131.8		-	-	d^6 DMSO
Pt(O-MDPIPBAH)Cl	164.2	135.2	146.8	128.7	129.0	128.1	-	-	126.1	126.0	132.0	-	127.2	146.3	127.2	125.6	130.5	CH 34.3 34.1	CH_2 24.6 24.4	$CDCl_3$
Pt(O-MDPBAH)Cl	-	135.7	-	127.2	126.4	127.6	127.8	-	126.7	125.7	124.7	125.6	128.4	-	124.8	129.1	124.4	-	-	$CDCl_3$

Key: all values p.p.m. relative to TMS.

^{19}F N.M.R.

Complex	Signals
Pd(O-MDPFPBAH)Cl	-117.63, 120.97

Key: values relative to $CFCl_3$

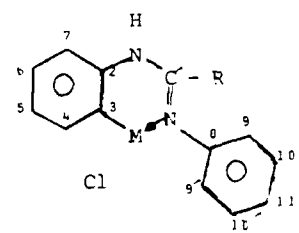


Figure 5.7

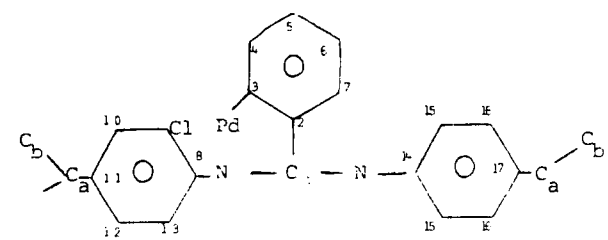
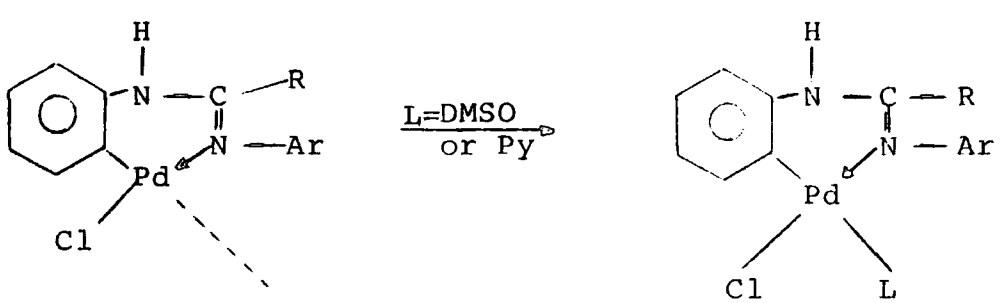


Figure 5.8

and a similar one to the related *ortho*-metallated rhenium *e.g.* 3340 cm^{-1}.[13] The acetamidine and formamidine complexes may only form six-membered ring complexes, whereas the benzamidines may form five, six ring, or a mixture of both complexes. Study of the ν(N-H) vibration (Table 5.2) shows that in the infra-red spectra there is no correlation between ν(N-H) position and ring size, *e.g.* $[Pd(O\text{-}M\ DPAAH)Cl]_n$, 5-membered ring ν(N-H), 3320 cm^{-1}, $[Pd(O\text{-}M\ DPFAH)Cl]_n$, 5-membered ring ν(N-H), 3240cm^{-1}. The position of the vibration actually changes depending on the solvent from which the complex is recrystallised, *e.g.* $[Pd(O\text{-}M\ DPIPBAH)Cl]_n$; from reaction mixture ν(N-H) 3330 cm^{-1}, from a D.M.S.O. recrystallisation 3360 cm^{-1}. This may be attributed to the breaking down of large aggregates by highly donating solvents and consequent breakdown of any H-bonding and packing factors which may affect the position of the ν(N-H) signal. The break-up of the structure would be achieved by the cleavage of the chlorine bridges in the complex, to form donor solvent adducts, *viz.*

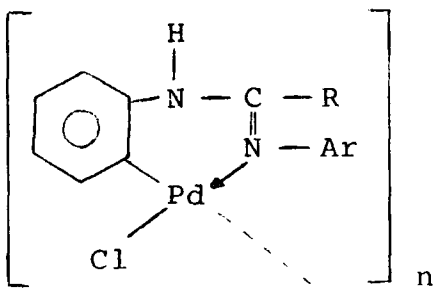


(Figure 5.9)

A similar effect has been noted in the mass spectrometer, where the mulling agent thiodiglycol cleaves the chlorine bridges (Figure 5.5). The infra-red spectra of all the complexes in the ν(NCN) region of the spectrum are complex. The highest frequency bands, assigned to the ν(NCN) asymmetric

stretch, are listed in Table 5.2, with the corresponding bands of the parent amidines. There is clearly a decrease in frequency compared with that of the parent amidine. This $\Delta\nu$ is attributed to the perturbation of the NCN group caused by the heavy Pd and Pt atoms.

The ^{1}H n.m.r. (Table 5.4) of the $[Pd(O\text{-}M\ DPAAH)Cl]_n$ and $[Pd\ (O\text{-}M\ DPAAH)Cl]_n$ are clearly consistent with a structure of the type (Fig. 5.10):



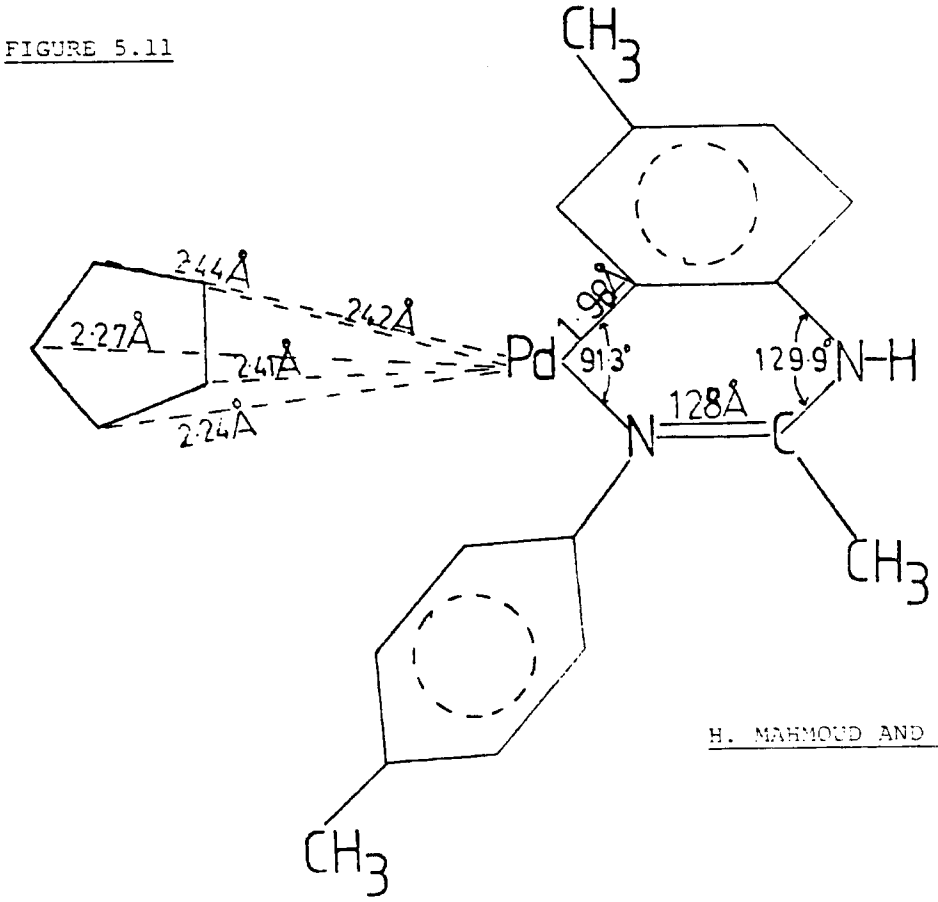
(Figure 5.10)

which is analogous to the complex previously synthesised by Kilner,[14] and which as a cyclopentadiene derivative Wallwork [15] found unequivocally to have a six-membered ring system by X-ray crystallography (Figure 5.11). The benzamidine *o*- metallated complexes have ^{1}H n.m.r. spectra with very complex aromatic regions, however the substituent groups on the nitrogens, *e.g.* CH, and CH_3 in the case of $[Pd(O\text{-}M\ DPIPBAH)Cl]_n$ give rise to two signals in each case which is expected for an *o*-metallated structure. Similarly the ^{19}F n.m.r. of $[Pd(O\text{-}M\ DPFPBA)Cl]_n$ has two signals present. Interestingly the N-H signals for the benzamidine complexes occur at lower fields than those of the acetamidine and formamidine complexes, and may be indicative of a five-emembered rather than a six-membered ring system (Table 5.4).

The ^{13}C n.m.rs. of the complexes were very difficult to obtain because of poor solubility, and in the main the result

π-CYCLOPENTADIENYL-N,N'-DI-P-TOLYLACETAMIDINO PALLADIUM

FIGURE 5.11



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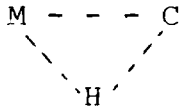
was a few signals which were attributable to the aryl rings. However, reasonable spectra were obtained for $[Pd(O\text{-}M\ DPIPBAH)Cl]_n$ and $[Pd(O\text{-}M\ DPAAH)Cl]_n$ which were comparable. The C-1 signal (see Figure 5.8) appears at a lower field in the benzamidine case (163.5 p.p.m.), than the acetamidine case (156.2 p.p.m.). This may be indicative of five- and six-membered ring structures respectively. The five-membered ring allowing more delocalisation over the C-1 carbon, and hence a downfield shift. The *ortho*-metallated C-3 carbon (Figure 5.8) of the aryl ring is moved downfield to a considerable extent, *e.g.* Δ p.p.m. $[Pd(O\text{-}M\ DPAAH)Cl]_n$, Δ = 23 p.p.m. and $[Pd(O\text{-}M\ DPIPBAH)Cl]_n$, Δ = 14 p.p.m.

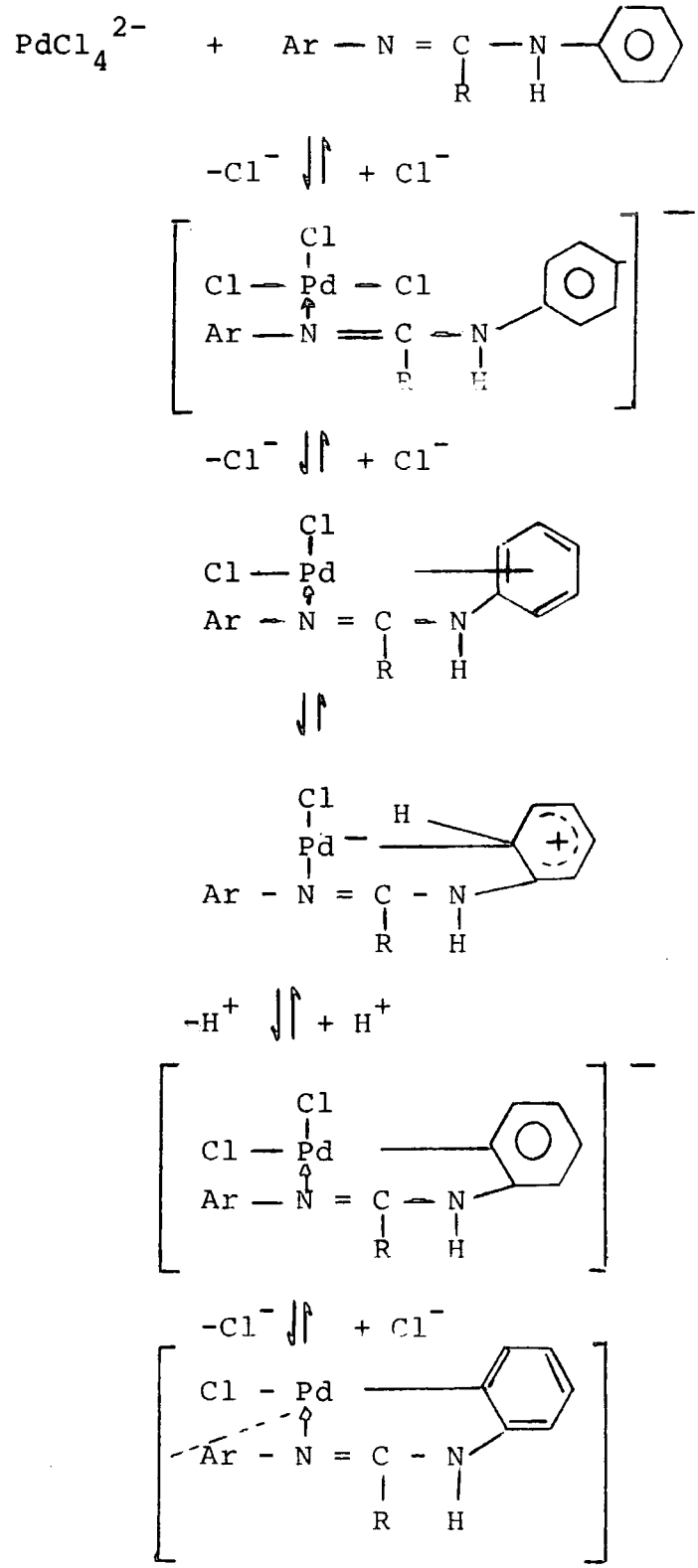
The complexes are similar in nature to the *ortho*-metallated azobenzene palladium and platinum complexes[4] and the mechanism of formation is probably similar to that described by Parshall[1] for azobenzene, (Fig.12).

Steps I and II may either occur by an SN1 or an SN2 mechanism, and an analogous azobenzene complex to that postulated in step I has been isolated.[16] The significant interaction in the sequence occurs in II, with the formation of a π-arene complex. The exact nature of steps III to IV is unknown, but a three centre intermediate has been postulated, *viz:*



(Figure 5.13).

FIGURE 5.12 Proposed Mechanism of formation of Palladium and Platinum *ortho*-metallated Complexes.



The platinum complexes will be formed in a similar manner. The nickel complexes were produced by the effect of heat, and could not be purified in the time available, although infra-red data confirmed the presence of an *ortho*-metallated species. The main impurity was unreacted nickel chloride, and this may be removed in the future by soxhlet extraction with monoglyme, or washing with alcohols: the very insoluble *ortho*-metallated species being isolated as a residue. The yellow residue from the palladium reaction was very involatile, and difficult to recrystallise, spectroscopic and infra-red analysis indicated unreacted amidine, $Pd(Am\ H)_2Cl_2$ and palladium hydroxide as being present.

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CHAPTER SIX

THE REACTION OF LITHIATED UNSUBSTITUTED AMIDINES WITH $M(PhCN)_2Cl_2$ (M=Pd or Pt)

6.1 Introduction

In previous chapters we have investigated the reactions of lithiated aryl substituted amidines with $M(PhCN)_2Cl_2$ (M = Pd or Pt) complexes and anhydrous nickel chloride; as well as the reactions of neutral amidines with tetrachloro-palladate and platinate salts. This chapter describes the reaction of lithium derivatives of unsubstituted amidines of the type Li[HNC(R)NH] [R= Ph, t-but) with $Pt(PhCN)_2Cl_2$ and $Pd(PhCN)_2Cl_2$.

6.2 The Reaction of $Pt(PhCN)_2Cl_2$ with Li[HNC(Ph)NH]

Benzamidine hydrochloride (previously dried), (1.5552g.; 10 mmols) was dissolved in anhydrous diethyl ether (100 ml.) to yield a white suspension. The suspension was cooled to 0^oC. with an ice bath, and n-butyl lithium (20 mmol.; 2.65 mls.) added. The solution was cooled to -196^oC using liquid nitrogen, and $Pt(PhCN)_2Cl_2$ (2.3607g.; 5 mmols) added. The mixture was stirred for 48 hours at room temperature yielding a yellow solution. The solvent was removed *in vacuo*, and the residual recrystallised from dichloromethane (200 ml.), to yield golden yellow platelets of $Pt[HNC(Ph)NC(Ph)NH]_2$. Yield: 84%, m.p. 98^oC decomposed.

6.2.1 Analytical Data

Found: C, 52.81; H, 4.91; N, 13.03; Pt, 27.6%.

$PtC_{28}N_6H_{24}$ requires C, 52.59; H, 3.76; N,13.14; Pt, 30.51

6.2.2 I.R. data (CsI/KBr plates; nujol/hexachlorobutadiene mulls) for $Pt[HNC(Ph)NC(PhNH]_2$

3420(w), 3220(br.m.), 3040(w), 2960(w.sh.), 2860(2), 2160(v.w.), 1630(m.), 1582(w), 1560(w), 1530(s), 1450(s), 1420(s), 1300(m), 1260(w.sh.), 1040(w), 1030(w), 1000(v.w.), 920(m.br.), 840(w.w.br.), 790(w.sh.), 780(m), 720(s.sh.), 698(v.s.), 590(v.w.).

Key: w=weak, m=medium, s=strong, sh=shoulder, v=very, br=broad.

6.2.3 Mass Spectrum

TABLE 6.1 Mass Spectral Fragmentation Assignment for $Pt[HNC(Ph)NC(Ph)NH]_2$

Peaks m/e	Assignment
639	$^{195}PtC_{28}N_6H_{24}$
536	$^{195}PtC_{21}N_5H_{19}$
417	$^{195}PtC_{14}N_3H_{12}$
314	$^{195}PtC_7N_2H_7$
119	$PhCN_2H$
103	PhCN

6.2.4 N.M.R. Data (Tables 6.2 and 6.3)

TABLE 6.2 ^1H N.M.R. Spectrum of $Pt[HNC(Ph)NC(Ph)NH]_2$

δ value p.p.m.	Integral	Assignment
8.25 - 7.38 complex multiplet	20(H)	Phenyl hydrogens
8.8	-	N-H protons? (very weak)

TABLE 6.3 ^{13}C N.M.R. Spectrum of Pt [HNC(Ph)NC(Ph)NH]$_2$

Carbon Assignment p.p.m. Figure 6.1					
C-1	C-2	C-3	C-4	C-5	Other weak signals
157.6	139.2	128.0	124.9	126.9	at 128.3, 129.25, 131.8

All values relative to T.M.S. = 0, Solvent $CDCl_3$

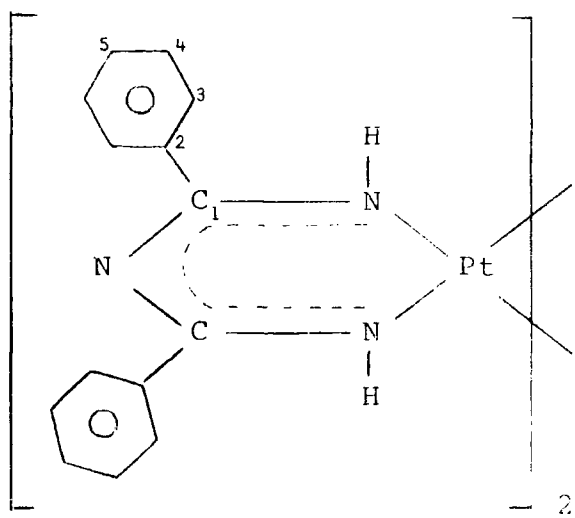

Figure 6.1

6.3 The Reaction of $Pd(PhCN)_2Cl_2$ with $Li[HNC(C_4H_9)NH]$

T-butylamidine HCl (0.6755g.; 0.5 mmols) was dissolved in monoglyme (100 ml.) to yield a white suspension. This was cooled to 0°C using an ice bath, and n-butyl-lithium (6.62 ml.; 10 mmol.) added. The solution became white in colour, and a suspension formed. After stirring for $^3/_4$ hr. at room temperature the suspension was cooled to -196°C with

liquid nitrogen, and $Pd(PhCN)_2Cl_2$ (0.0958g.; 0.25 mmol) added. The solution was allowed to stir for 14 hrs. at room temperature yielding a bright-yellow solution. The solvent was removed *in vacuo* to yield a yellow-green solid. The solid which proved fairly insoluble, was washed with diethyl ether (160 ml.) and then dichloromethane (100 ml.), before recrystallisation from T.H.F. (150 ml.) to yield a lemon solid (mp 146°). A small amount of T.H.F. insoluble red-brown solid was removed by filtration.

6.3.1 Analytical Data

Found: C, 43.02; H, 8.52; N, 13.59 $[PdC_{24}N_6H_{32}]_n$ requires C, 56.45; H, 6.27; N, 16.43 Pd, 20.84.

6.3.2 I.R. Data (CsI/KBr plates, nujol and hexachlorobutadiene mulls) for $Pd_n[HNC(t\text{-but})NC(Ph)NH]_{n+1}$

3390(br.s.), 2960(s), 2920(s), 2860(s.sh.), 1630(s), 1580(m), 1550(s), 1450(m), 1370(m), 1250(m), 1230(m.sh. 1250(m), 1230(m.sh), 1198(w), 1025(w), 970(w), 860(w), 800(w), 600(s.br.), 530(v.br).

6.3.3 Mass Spectrum

TABLE 6.4 Mass Spectral Fragmentation Assignment for $Pd_n[HNC(t\text{-but})NC(Ph)NH]_{n+1}$

Peaks m/e	Assignment
1126	$^{106}Pd_3C_{48}N_{12}H_{64}$
818	$^{106}Pd_2C_{36}N_9H_{48}$
715	$^{106}Pd_2C_{29}N_8H_{43}$
616	$^{106}Pd_2C_{24}N_6H_{32}$
510	$^{106}PdC_{24}N_6H_{32}$
308	$^{106}PdC_{12}N_3H_{16}$
205	$^{106}Pt[C_4H_9C(NH)_2]$
103	PhCN
99	$C_4H_9(NH)_2$

6.3.4 N.M.R. Data (Tables 6.5 and 6.6

TABLE 6.5 ^1H N.M.R. Data of $Pd_n[HNC(t\text{-but})NC(Ph)NH]_{n+1}$

δ values p.p.m.	Integral	Assignment
1.51	9H	t-butyl group
1.58		t-butyl group
7.71-8.3 complex multiplet	5H	PhCN

All values relative to T.M.S. = 0 p.p.m. Solvent $CDCl_3$

TABLE 6.6 ^{13}C N.M.R. Data of $Pd_n[HNC(t\text{-but})NC(Ph)NH]_{n+1}$

C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
n.o.	132.2	129.2	127.3	128.7	175.9	37.2	28.2
Other weaker signals at 29.0, 176[t-butylHCl] and 132.8, 130.0 and 128.85							

All values relative to T.M.S. = 0, Solvent $CDCl_3$; n.o.=not observed.

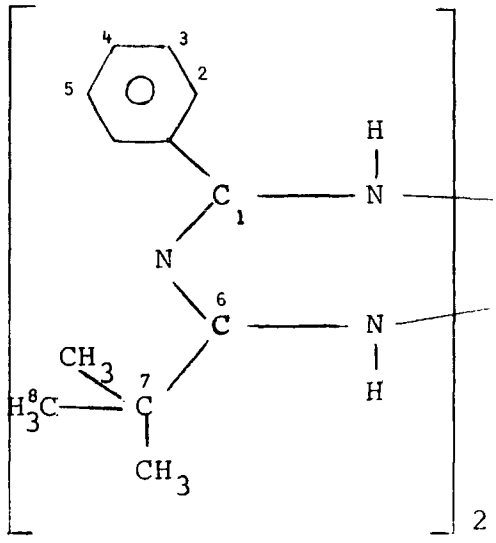

Figure 6.2

6.4 Discussion

Lithiated benzamidine has reacted with $Pt(PhCN)_2Cl_2$, by nucleophilic attack at the nitrile to yield $Pt[HNC(Ph)NC(Ph)NH]_2$, a platinum complex containing two six-membered rings. The structure has been proven unequivocally by Wallwork[1] using X-ray crystallography, and is described in Figure 6.3. The $Pt[HNC(Ph)NC(Ph)NH]_2$ complex is a golden-yellow crystalline solid which is stable in air over short periods as a solid, but decomposes rapidly in solution. The $Pt[HNC(Ph)NC(Ph)NH]_2$

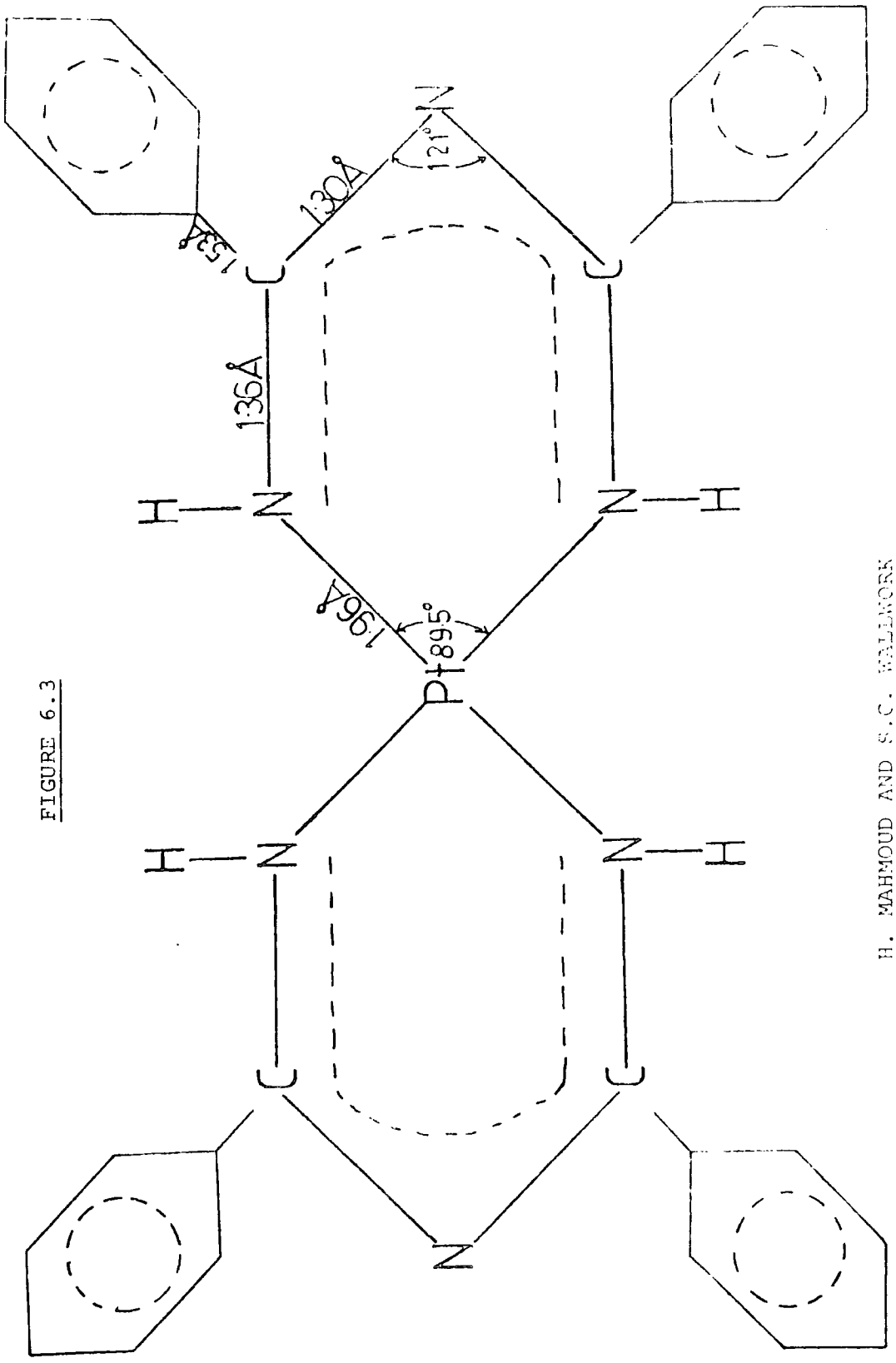

FIGURE 6.3

H. MAHMOUD AND S.C. WALLWORK

complex is similar to those described previously by Kemmit[2] shown in Figure 6.4, and by Bruce and Woodward[3], Figure 6.5,

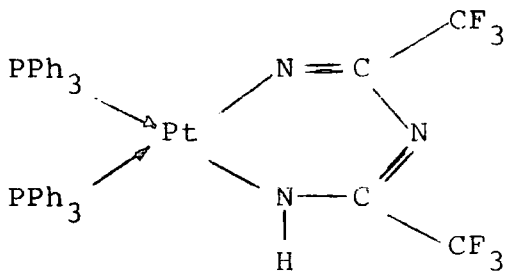

Figure 6.4

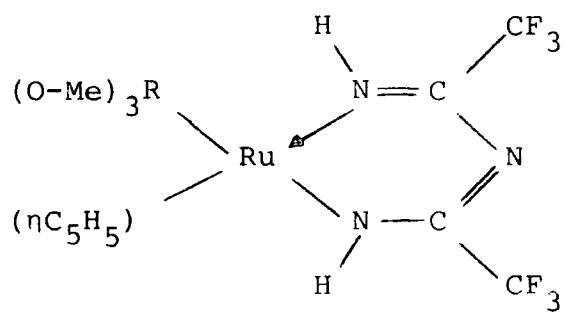

Figure 6.5

which have been characterised by X-ray crystallography, as can be seen by comparing the structural parameters described in Table 6.7.

TABLE 6.7 Comparison of Structural Parameters of Complexes containing Six-membered Rings

Structural Parameter	$Pt[HN(Ph)NC(Ph)NH]_2$ (1)	$(PPh_3)_2Pt(HNC-(CF_3)NC(CF_3)N)$ (2)	$[P(OMe)_3(\eta C_5H_5)]Ru-(HNC(CF_3)NC(CF_3))(NH)$ (3)
M-N	1.96	2.02	2.07 Å
(M)-N-C	1.36	1.36 and 1.24	1.27 and 1.29 Å
C-N-(C)	1.30	1.34 and .32	1.32 Å
C-$\hat{N}$-C	121	-	119.5°
N-$\hat{M}$-N	89.5	-	83.6°

For Pt[HNC(Ph)NC(Ph)NH], the $\nu(N-H)_{str.}$ bands at 3420 and 3320 cm^{-1} are higher than those of the parent amidine at 3290 and 3220 cm^{-1}. It should also be noted that in nujol mull the complex was very susceptible to hydrolysis. The $\nu(N-C-N)$ asymmetric structure vibration of the parent (1640(s.br.) cm^{-1}) is slightly lowered in frequency, *c.a.* 1630 (s.br.) cm^{-1} and reduced in intensity on complexation.

The ^{1}H n.m.r. has a complex multiplet in the aromatic region as expected, and a very weak signal at *c.a.* δ8.8 which may be attributable to the N-H protons. The ^{13}C n.m.r. (Fig. 6.1) is assignable in accordance with the X-ray structure (Fig.6.3), though the aromatic region of the spectrum is more complex than expected with three extra signals being observed. There are several possible explanations for these signals. One is that at room temperature the rotation of the aryl rings is slow, and hence we are not seeing time averaged aryl environments. Another possibility is the introduction of asymmetry into the complex, however, this would involve additional peaks being observed for C-1 and C-2 carbons (Fig.6.1), which is not the case. Sample decomposition, or tautomerism of the central ring would have a similar effect. None of these explanations may be used to fully explain the observed data. The C-1 carbon is moved only slightly upfield on complexation when compared with the C-1 in benzamidine 164.6 p.p.m.[4] The upfield shift may be due to a greater spreading of the electron-delocalisation associated with this carbon in the free amidine, throughout the new ring system.

The parent ion of the complex is observed in the mass spectrum at m/e 639. The breakdown of the complex occurs by the break-up of one of the rings resulting in the loss of PhCN, followed by the break-up of the other ring, again resulting in PhCN loss, and leaving the two amidine fragments joined to the platinum. Finally both fragments are lost.

Lithiated t-butyl amidine has reacted with $Pd(PhCN)_2Cl_2$ in a similar manner to the reaction of lithiated benzamidine and $Pt(PhCN)_2Cl_2$, to yield a lemon air and moisture sensitive product. Analysis (presence of chlorine), and n.m.r. (signals due to t-butyl amidine HCl), show that the product contains unreacted amidine, probably arising from incomplete reaction of the amidine at the lithiation stage. The complex is also fairly insoluble, and numerous recrystallisations failed to produce uncontaminated product. Attempts at chromotographic separation were precluded by poor solubility. The mass spectrum indicates $Pd_3[HNC(t\text{-but})NC(Ph)NH]_4$ species, and shows a ligand ring breakdown pattern similar to that observed for $Pt[HNC(Ph)NC)Ph)NH]_2$. The ^1H n.m.r. of the complex shows one peak associated with the t-butyl portion of the composite ligand, and complex multiplet for the aromatic ring. A weak signal associated with unreacted starting material was observed at δ1.58 p.p.m. The ^{13}C n.m.r. contains signals consistent with a $Pd_n[HNC(t.but)NC(Ph)NH]_{n+1}$ complex, although as in the case of $Pt[HN\text{-}C(Ph)NC(Ph)NH]_2$, the aromatic region contains some complications. The C-1 (Fig.6.2) carbon was not observed. The C-6 (Fig.6.2) ring carbon associated with the t-butyl group is moved slightly upfield when compared with that of t-butyl amidine hydrochloride (176.95 p.p.m.), indicatin

that delocalisation throughout the composite ligand is occurring, causing the electron density at the C-6 carbon to be reduced slightly. The i.r. data did not yield useful data because of contamination by unreacted ligand.

The mass spectral for $Pd_n[HNC(t\text{-but})NC(Ph)NH]_{n+1}$ is especially useful in indicating a possible formulation. The complex is clearly not of the $M(L)_2$ type observed for $Pt[HNC(Ph)NC(Ph)NH]_2$. Two possibilities are: Figs.6.6, 6.7,

(1) A polymer:

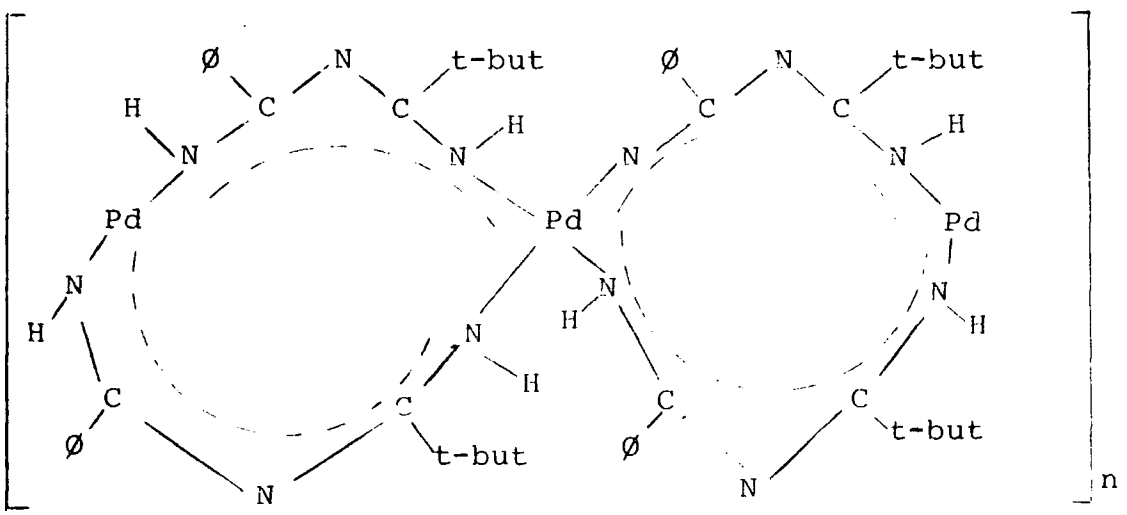

Figure 6.6

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(2) A trimeric structure based on palladium(II) acetate (5).

The latter structure does, however, presume that the parent ion is not observed in the mass spectrometer, but that of the parent-2 ligands. This would not be surprising considering the high mass of the postulated complex.

(See Figure 6.7 on following page).

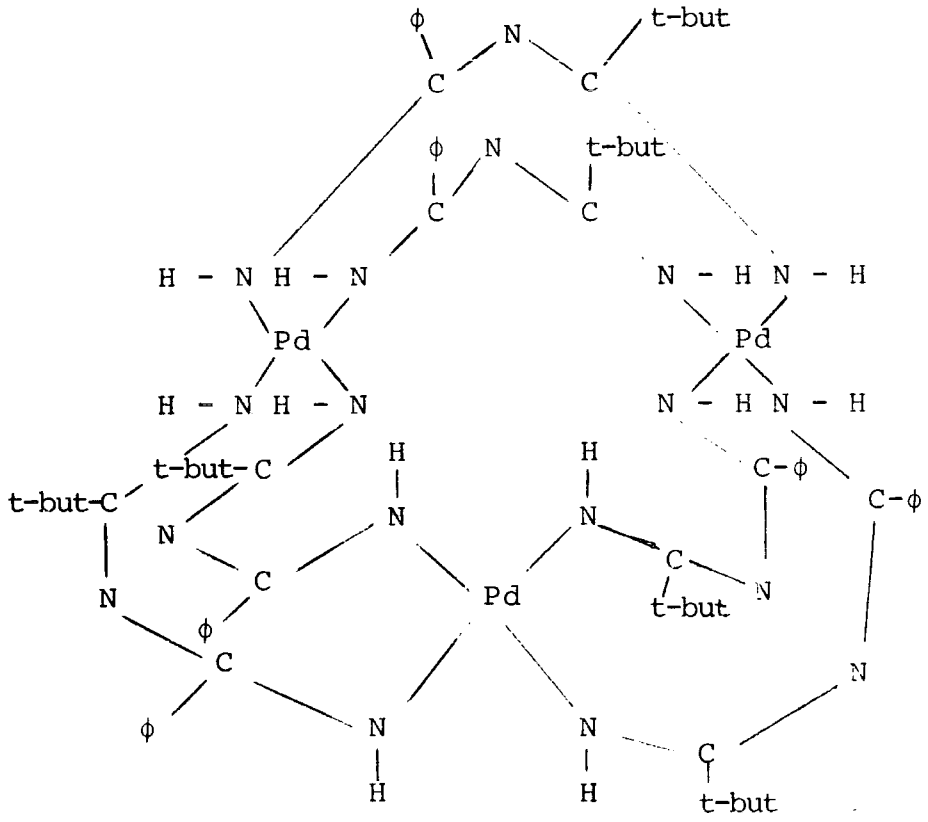
ϕ
N
t-but
C
C
ϕ
N
t-but
C
C
H - N H - N
N - H N - H
Pd
Pd
H - N H - N
N - H N - H
t-but-C
H
H
C-ϕ
t-but-C
C-ϕ
N
N
N
C
N
Pd
C
N
t-but
ϕ
C
N
ϕ
N
N
C
H
H
t-but

Figure 6.7

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APPENDIX A

EXPERIMENTAL DETAILS

A1.1 Techniques:

1.1.1 General

Before use all solvents were rigorously degassed. Reactions were carried out in two-necked flasks or single Schlenk tubes. Solutions were transferred either by syringe against a counter-current of nitrogen or *via* Schlenk capillary needles and a positive nitrogen pressure. The manipulation of solid air sensitive materials was carried out in a glove box.

1.1.2 Nitrogen Supply

The nitrogen supplied to the bench, the boil off from the department's liquid nitrogen plant, was passed over a hot upper catalyst to reduce the content to less than 10 p.p.m. The supply was bubbled through concentrated H_2SO_4 and passed through two P_4O_{10} towers before use at the bench. A constant pressure of nitrogen was maintained in the system by the connection of one outlet to a bubbler containing heavy white oil.

1.1.3 Glove box

The purity of the nitrogen in the glove box was maintained by continuous recycle through a P_4O_{10} column. The transfer ports were flushed with this nitrogen. A crystallising dish containing fresh P_4O_{10} was always kept in the box, again to keep the water content to a minimum. All external tubing was of P.V.C. or glass. The atmosphere was found to be suitable for manipulations of the complexes; however for long term storage the complexes were stored in sealed mini Schlenk tubes to prevent slow decomposition.

1.1.4 Vacuum Line

A vacuum line was fitted with two-way taps connected to the nitrogen supply, allowing apparatus to be alternatively degassed and filled with nitrogen, thus creating and maintaining an inert atmosphere. The line was connected to a rotary vacuum pump and was capable of maintaining a vacuum of O.Olmm.Hg.

1.1.5 Chromatography

Column chromatography was employed to purify some products. The column was fitted with a jacket to allow cooling and handling the more thermally unstable products. The column was degassed by bubbling nitrogen vigorously through the column/solvent slurry for several minutes. Transfer of solutions was carried out by using Schlenk needles, a constant pressure of nitrogen being used at all times.

A1.2 Instrumentation:

1.2.1 Mass Spectroscopy

Electron-impact mass spectra were obtained on A.E.I. MS9 mass spectrometer operating at 70eV with an accelerating potential of 8kV., and a source temperature of 200^{o}C. Samples were mounted on an inert ceramic and introduced by direct insertion into the ion source. Electron-impact positive ion, and negative ion mass spectra, and chemical ionisation mass spectra were obtained on a VG 7070E mass spectrometer. Samples were introduced *via* glass capillaries, and the sample volatilised by a variable-temperature probe tip. A variety

of standards were used to calibrate the instruments, *e.g.* perfluorokerosene. Ammonia and iso-butane were used as gases for the negative ion, and chemical ionization techniques. Fast-Atom-Bombardment (F.A.B.) positive ion mass spectra were obtained on VG ZAB-1F mass spectrometer at PCMU Harwell. A variety of mulling agents were used (*e.g.* glycerol).

1.2.2 Thermal Analysis

Thermo-gravimetric analysis traces were recorded on Stanton Redcroft TG750 and 760 instruments. Air-sensitive samples were put into platinum crucibles in the glove box, and then transferred to the instrument in a nitrogen filled bottle. A small amount of exposure to air occurred during transference of the crucible to the instrument; hence the error of 1-2% of a percentage weight loss, normally associated with this technique was extended to 3%.

1.2.3 Infra-red Spectroscopy

Infra-red spectra in the range 4000 cm^{-1} - 200 cm^{-1} were recorded on a Perkin-Elmer 577 grating spectrophotometer. Nujol and hexachlorobutadiene mulling agents were used, in conjunction with caesium iodide and potassium bromide plates. A solution cell with potassium bromide plates and 0.1mm spacers was also used.

1.2.4 Nuclear Magnetic Resonance Spectroscopy

A variety of spectrometers were utilised, the nature and properties, particularly solubility of the complex determining which instrument was used. Proton n.m.r. spectra were recorded on a Varian E.M. 360L spectrometer. A Bruker

HX90E spectrometer modified for F.T. operation using a Nicolet B.N.C. 12 computer was used for ^{1}H n.m.r., ^{19}F n.m.r. and ^{13}C n.m.r. A Bruker WH300 spectrometer at the University of Newcastle upon Tyne was used to record ^{1}H and ^{13}C spectra, and ^{13}C spectra were also recorded on a Bruker WH360 spectrometer at the University of Edinburgh. A variety of solvents were used and $(CH_3)_4Si$ was employed as an internal reference.

1.2.5 Raman Spectroscopy

Attempts to record the spectra of the complexes using a Cary 82, 180° geometry laser Raman spectrometer utilising a Spectraphysics 164 argon ion laser failed because of fluorescence/decomposition problems.

1.2.6 Melting Points

These were determined using a Gallenkamp capillary melting point instrument.

1.2.7 Gel Permeation Chromatography

A Perkin-Elmer 601 gel-permeation chromatograph was used with a Knaur differential diffractometer. Three columns were used in the series, the pore size decreasing $10^5 \longrightarrow 10^3 \longrightarrow 500$Å. Polystyrene gel columns and sample ran as a 0.5% polymer solution in T.H.F. plus 2,6,tri-t-butyl-phenol (peroxide inhibitor).

1.2.8 E.S.C.A.

(S.A. Johnson, University of Durham); the samples were placed on double-sided scotch tape and an A.E.I. ES 200B Electron Spectrometer used to obtain the data.

1.2.9 G.C./M.S.

This was carried out on a VG Micromass 12 instrument, coupled to a Perkin-Elmer 104 gas chromatograph.

A1.3 Analysis:

1.3.1 Carbon, Hydrogen and Nitrogen

These were obtained using a Perkin Elmer 240 Elemental Analyser. In some cases incomplete combustion was noted, a problem which was partly solved by the addition of vanadium pentoxide to the sample before combustion.

1.3.2 Halogens

Chlorine was determined using the conventional method of oxygen flask combustion followed by potentiometric titration of the halogen ion. Fluorine was determined by

fusion with potassium followed by titration with sodium hydroxide.

1.3.3 Metals

Metal analysis was undertaken using a Perkin-Elmer 403 A.A. spectrometer. Problems with reliability were found because of cloudy precipitates formed even in aqua-regia solutions. In many cases metal content was taken as the residue from thermal analysis of the sample. The residues were proven to be platinum or palladium metal by atomic absorption spectrometry.

A1.4 Preparation and Purification of Starting Materials:

1.4.1 Hydrocarbons and diethyl Ether were dried over freshly extruded sodium wire. Monoglyme and T.H.F. were dried by refluxing for 48 hours over potassium, then distillation under nitrogen and storage over freshly extruded sodium wire. Dichloromethane and chloroform were distilled under nitrogen and stored over activated 3A molecular sieve. Benzonitrile was distilled under reduced pressure, the fraction of b.p. >161^{o}C being collected over 3A molecular sieve.

1.4.2 Preparation of platinum and palladium bis-benzonitrile dichlorides

A typical preparation was carried out as follows, and was based on the method given by Marr[1] . Benzonitrile (15 ml.) and palladium chloride (0.4 g.) were placed in a double-necked flask fitted with a water condenser. The solution was warmed to 100^{o}C for several hours until all the

palladium chloride dissolved. Extreme care was used to prevent the solution temperature becoming > 100°C as decomposition then occurs. Whilst still hot the solution was filtered into a second flask containing 30/40 petroleum ether (100 ml.). The product $Pd(PhCN)_2Cl_2$ precipitated immediately, and was separated by filtration, washed with hexane (3 x 20 ml.) and then dried *in vacuo*. The remaining liquor was concentrated by warming under *vacuo*. More 30/40 petroleum ether (40 ml.) was added and the solution cooled (-16°C) to yield more product. This process was repeated until no more product could be obtained. Yield 95-98%.

Typical analysis

$Pd(PhCN)_2Cl_2$: found %C = 43.89, N = 7.06, H = 2.61
requires %C = 43.85, N = 7.30, H = 2.61.

$Pt(PhCN)_2Cl_2$: found %C = 36.29, N = 5.22, H = 1.72
requires %C = 35.61, N = 5.93, H = 2.18.

1.4.3 Preparation of anhydrous nickel chloride (0.3 1,2-Dimethoxyethane)

A flask was fitted with a reflux condenser and purged with nitrogen. Powdered nickel chloride hydrate (21.66g, 131 mmol), dry monoglyme (65.5 ml.) and peroxide free triethyl orthoformate (47.8 ml.) were refluxed for two hours. On cooling the yellow, granular product $NiCl_2$ 0.3 $C_4H_{10}O_2$ was removed by filtration, washed with monoglyme and pentane and dried *in vacuo*.

$NiCl_2O.3C_4H_{10}O_2$ found %Ni = 34.55, Cl_2 = 45.24, C = 8.88, H=1.94
requires %Ni = 37.49, Cl_2 = 45.27, C = 9.20, H=1.90

1.4.4 Amidines

Diphenylacetamidine was obtained from Eastman Kodak Organic Chemicals and used without further purification, other amidines were prepared using variations of literature methods (2,7). For example:

1.4.4.1 Preparation of N,N´di-p-isopropylphenylbenzamidine

N-iso-propylbenzamide (111.07g., 0.465 mmol) in toluene (1000 ml.) was cautiously added to phosphoruspentachloride (136.57g, 0.655 ml.) in a flask fitted with a water condenser. After heating for 1 hr. iso-propyl aniline (63.56 ml. 0.465 mol) in toluene (250 ml.) was added. Reflux was continued for a further four hours. The solution was cooled in an ice bath and then filtered. The resultant pale yellow solid after washing with cold toluene and hexane, was dissolved in the minimum quantity of hot diethyl amine (∿300 ml.) and filtered into a large excess of cold distilled water (*ca.* 3,500 mls.). After the solution was stirred overnight, the precipitate was separated by filtration, washed with distilled water and recrystallised from ethanol/water. Ivory crystals were isolated. Yield = 24%.

$Pr^{i}C_6H_4N(H)C(Ph)NC_6H_4Pr^{i}$ found % C=84.56, N=7.36, H=8.82
requires % C=84.28, N=7.86, H=7.86.

1.4.4.2 Preparation of N,N´di-p-tolylbenzamidine

Phosphorus pentachloride (168.29g., 0.808 mol), and a slurry of N-p-tolylbenzamide (158.25g., 0.75 mol) in toluene (1,500 ml.) were cautiously mixed as described in Section A.1.4.4.1. After heating to reflux for 1 hr., p-toluidine

(8.37 g., 0.75 mole) in toluene (800 mls.) was carefully added and the resultant bright yellow solution was refluxed for a further four hours. The yellow precipitate obtained on cooling was separated by filtration, washed with toluene and hexane, and dissolved in the minimum amount of hot diethylamine. On pouring into cold distilled water, the product precipitated. Recrystallisation was achieved using ethanol/water mixture at $-16^{o}C$. Yield = 23%.

$p\text{-}CH_3\text{-}C_6H_4N(H)C(Ph)NC_6H_4\text{-}CH_3\text{-}p$ found % C=84.05, N=8.11, H=7.60
requires % C=84.01, N=9.33, H=6.66.

1.4.4.3 Preparation of N,N´di-p-fluorophenylbenzamidine

Reaction procedure was similar to that found in 1.4.4.1. Phosphorus pentachloride (156.38g., 0.75 mole), a slurry of N-p-fluorophenylbenzamide (133.07 g., 0.6189 mole) in toluene (1000 ml.), and p-fluoroaniline (58.65 ml. 0.6189 mole) in toluene (200 ml.) were used. White crystals were isolated from the ethanol water mixture. Yield = 34%.

$p\text{-}F\text{-}C_6H_4\text{-}N(H)C(Ph)N\text{-}C_6H_4\text{-}F\text{-}p$ found % C=73.85, N=8.54, H=5.71, F=12.11
requires % C=74.04, N=9.09, H=4.54, F=12.33

1.4.4.4 Preparation of N,N´dimethylbenzamidine

N-methyl-p-toluenesulphonamide (21.9 g., 118.25 mmol), and benzoic acid (7.21 g., 59 mmol) were heated to $\sim 235^{o}C$ but once the reaction was under way this was ceased. The reaction temperature rose to over $280^{o}C$ and then dropped to $235^{o}C$. This temperature was maintained for *ca.* 15 minutes, and the reaction mixture was then cooled to $\sim 80^{o}C$ with stirring.

Distilled water (∿100 ml.) was added to dissolve the raw black product mixture. On cooling to room temperature the solution was made strongly alkaline and the product extracted with chloroform. Removal of the solvent by rotary evaporation yielded a residual liquid which was distilled under *vacuo* to yield the white product, on cooling to room temperature. Yield = ∿30%. (This varied dramatically from one preparation to another, in one case no product was isolated).

$CH_3=N(H)C(Ph)N-CH_3$ found % C=72.40, N = 18.34, H = 8.67.

requires % C=72.99, N = 18.91, H = 8.1.

The ligand was unstable at room temperature and hydrolysed rapidly.

A1.5 Other reagents

Unless specified in the text all other chemicals were used as supplied by the manufacturer without further purification.

APPENDIX A - REFERENCES

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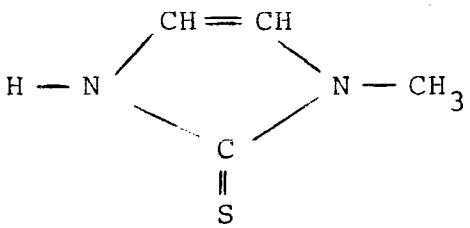
APPENDIX B

THE REACTION OF BIS(N,N´DIPHENYLBENZAMIDINO)PLATINUM(II) WITH 1-METHYL IMIDAZOLINE-2-THIONE

B.1 Experimental

A mixture of $Pt(DPBA)_2$ with 1-methyl-imidazoline-2-thione (0.057.05g.; 0.5 mmol) (Figure B.1), in T.H.F. (50 ml.), was refluxed for 1 hour yielding a green solution.



(Figure B.1)

The solution was reduced in volume *in vacuo* and cooled to $-16^{o}C$ for several hours. The resultant product was a green gum which proved intractable. After washing with pentane (20 ml.), the gum was dissolved in dichloromethane (20 ml.). Removal of the dichloromethane *in vacuo* whilst warming the vessel, resulted in the formation of a clear film on the sides of the Schlenk tube. Removal of the solvent was carried on to dryness, and the Schlenk tube rotated to build up the film on the sides. The vessel was warmed throughout the drying operation. When dry the film separated from the sides of the vessel, and was easily removed using tweezers. Attempts to purify the intractable gum which remained with a variety of solvents failed, as did attempts to produce more film from the addition of dichloromethane. A number of reactions were carried out to see if film formation occurred without one of the reactants being present. None were successful.

B.2 Elemental Analysis of the film

Found (%): C=41.11; H=6.39; Cl=50.1.

By the use of molar-ratio calculations, the empirical

formulation of the polymer in $C_{4.84}H_{9.04}Cl_2$. Hence, the bulk formulation of the polymer is approximately $C_5H_9Cl_2$. The analytical total indicates a mass deficiency of 2.4%.

$[C_5H_8Cl_2]_n$ requires (%) C = 43.22; H = 5.76; Cl = 51.02.

B.3 Mass Spectroscopy

It was necessary to heat the sample to obtain mass spectra, hence the fragments observed may be pyrolysis breakdown products of the polymer.

B.3.1 Positive ion-electron-impact mass spectrum

The spectrum was dominated by three peak clusters which were separated by 14 mass units in each case. These units make up the "$-CH_2$ backbone" of the polymer (Table B.1).

TABLE B.1 "$-CH_2$ backbone" mass spectral peaks positive ion

m/e	Assignment of Ions	% Intensity
41	C_3H_5	63
42	C_3H_6	18
43	C_3H_7	100
55	C_4H_7	56
56	C_4H_8	22
57	C_4H_9	92
69	C_5H_9	36
70	C_5H_{10}	15
71	C_5H_{11}	49
83	C_6H_{11}	25
84	C_6H_{12}	13
85	C_6H_{13}	30
97	C_7H_{13}	20
98	C_7H_{14}	12
99	C_7H_{15}	10

Higher peaks were noted at m/e 129 [22%], m/e 180 [29%] and m/e 284 [12%]. These higher peaks may simply be pyrolysis products.

TABLE B.2 "CH_2 backbone" mass spectral peaks - negative ion

Assignment of Ions	m/e	% Intensity
$C_{11}H_{16}$	148	51
$C_{14}H_{25}$	193	100
$C_{17}H_{21}$	225	38
$C_{18}H_{30}$	246	56
$C_{22}H_{33}$	297	91
$C_{28}H_{45}$	381	42
$C_{33}H_{56}$	452	87

B.4 Infra-red Spectrum (as film)

3400(v.w. br.), 2990 (s.sh), 2850 (v.s.), 2300 (s), 1724 (s), 1585 (v.s.), 1510 (v.sh.), 1440 (v.s. sh.), 1430 (v.s.), 1380 (w.), 1330 (m.), 1260 (v.s.br.), 1200 (w.), 1130 (w.), 1110 (m.), 1070 (m.), 970 (s.), 845 (m.), 750 (w.), 700 (s.br.), 640 (v.s.br.), 630 (v.s.br.), 410 (w.), 370 (m.) cm^{-1}.

B.5 Molecular Weight, by Gel-Permeation Chromatography

$\bar{M}_n$ = 1101 $\bar{M}_w$ = 1351

B.6 ^1H N.M.R.

C_6D_6 5.6 p.p.m. singlet.

B.7 Thermal Analysis

Three plateaux were noted in the thermogram.

TABLE B.3 Thermal Analysis Data

Temperature Range ^{o}C	% wt. loss
0 - 400	64
400 - 504	75
500 - 777	98

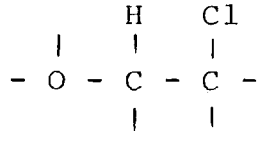
B.8 E.S.C.A. Data (S.A. Johnson, The University of Durham)

The wide scan spectrum indicated the presence of carbon, chlorine, silicon, and oxygen in/on the polymer surface. Some of these are attributable to silicon grease and vacuum pump oil (poly-phenyl ether), present as impurities on the sample. The sample loses chlorine under X-ray exposure, a behaviour analogous to that of P.V.C.; and builds up layers of hydrocarbon. The stoichiometry of the sample of the polymer was determined from the intensity and sensitivity ratios. For a unit of 24 carbons the following stoichiometry was found:

$$C_{25}Cl_5O_5Si_3$$

Assuming the grease to be $(Me_2SiO)_n$ then associated with the 3 silicon atoms there are 6 carbon atoms and 3 oxygen atoms. Thus, the polymer contains atoms in the approximate ratio $C_{18} : Cl_5 : O_2$. E.S.C.A. is a surface technique, and does not involve study of the bulk stoichiometry, and its application

is affected by the presence of vacuum pump oil, other surface contaminants and degradation of the polymer under the X-ray beam. The formulation given is for the surface of the polymer, and not the bulk. The binding energies suggested the presence of the following groups, C-O, C-Cl, and small amounts of CCl_2, though the peak at 288.2eV could not be confidently attributed to CCl_2 rather than C=O. Interestingly the absolute binding energy of the $2p^3/2$ state of Cl2p spectrum is very similar to that of P.V.C. The presence of either ether or hydroxyl linkages in the chain would lead to different numbers of C-O links. For example, in a unit of 24 carbon atoms there would be four C-O linkages present if the C-O was present as an ether, and two if it was an hydroxyl. By estimating the area ratio expected for the 285.0eV (extraneous hydrocarbon) and 286.6eV peaks for each case and then comparing the results with that found experimentally, a hydroxyl linkage was deduced. However, the valence band spectrum was found to be similar to that of poly(epichlorohydrin), which contains ether linkages. E.S.C.A. studies of P.V.C.[1] show that X-ray degradation takes place by loss of chlorine as hydrogen chloride, and since loss of chlorine from the polymer is relatively rapid when compared with P.V.C., it suggests that some of the chlorine atoms are in a ß position with respect to the oxygen atoms, *viz.*

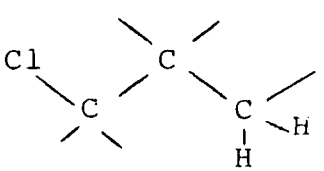


(Figure B.2)

in which the hydrogen is more acidic than those in P.V.C. and consequently the loss of hydrogen chloride is more facile.

Discussion

The polymer has a bulk formulation of $[C_5H_8Cl_2]_n$ based on elemental analysis, and gel-permeation chromatography measurements indicate an oligomer rather than a polymer. Mass spectral data indicates a long hydrocarbon backbone, the lack of Cl containing peaks being attributable to the lability of the chlorines under the thermal and electron-impact conditions found in the spectrometer. The polymer breaks down in the positive ion mass spectrum by step loss of m/e 14, attributable to $-CH_2-$ units. The thermogram indicates the polymer has a slightly higher thermal stability than polypropylene,polyethylene and P.V.C., but less than P.T.F.E.,[2] and the first % wt. loss (64%) is higher than would be expected theroetically for total hydrogen chloride loss from the polymer (52%) indicating backbone degradation is also occurring. The infra-red spectrum shows a number of bonds which may be assigned;[3] cm^{-1}: 2925 CH_2 asym.str., 2850 CH_2 sym. str., 1585 C-C-C str., 1430 $CH_{def.}$, 1260 CH_2 wag., 970 CH_2 wag olefinic, 650 C-Cl str. Assignment of the absorption at 650 cm^{-1} to ν(C-Cl) suggests that there is a hydrogen atom trans to the chlorine, *viz.*



(Figure B.3)

The proton n.m.r. was disappointing possibly due to the small sample size, the singlet at δ5.6 possibly being attributable to the $-CH_2-$ groups of the polymer. The data as a whole

indicates a long $[CH_n]$ n=1 or 2 oligomer containing -CH-Cl and possibly $-CCl_2-$ linkages. The E.S.C.A. surface and the chemical bulk analysis do not agree on the stoichiometry of the compound, but this is hardly surprising considering the degradation which it undergoes with X-rays. E.S.C.A. indicated the presence of C-O linkages in either hydroxyl or ether form as being present on the polymer surface, and it identified the fragment shown in Figure B.1, which is possibly present on the surface. However surface work of any kind is prone to problems, because of contamination of the surface being studied. The bulk analysis indicates that if oxygen groups are present then it would only be as a small amount, 2.4%. Thus, the oxygen containing species indicated by E.S.C.A. may indeed be in the polymer in small amounts, or it may simply be surface contamination. The polymer has a number of properties similar to P.V.C., *e.g.* loss of HCl on thermal or X-ray degradation, and hence may be regarded as having a similar structure to P.V.C., but with a reduced Cl content. The polymer is formed possibly from the reaction of T.H.F., and dichloromethane, presumably promoted by the platinum-amidine-imidazoline-2-thione catalyst. Analytical data approximates to a formulation $C_5H_9Cl_2$ which may represent a reaction of one mole of T.H.F. with one mole of CH_2Cl_2. Elimination of water would be necessary for such a reaction and may be the source of oxygen detected in the product by E.S.C.A. spectroscopy.

Reproducibility was a problem. A number of factors were found to be important in determining if polymer formation occurred: the reflux time, the molar-ratio of the catalyst

constituents, the drying of the polymer by warming, and the purity of the starting materials.

The catalyst itself was an intractable gum, and could not be identified. The positive and negative ion electron-impact mass spectra indicated the presence of 1-methyl-imidazoline-2-thione, platinum and amidine by detection of the species $[C_4N_2H_5S]^+$ m/e 113, $[C_4N_2H_7S]^+$ m/e 115, $[Pt]^+$ m/e 195 and $[DPBA]^+$ m/e 271. The colour and general properties of the material indicated a complex containing both thione and amidino groups. Platinum and amidine complexes are known to act as catalysts in a range of reactions but it has not been possible to identify the active ingredient in this system.

REFERENCES

1. D.T. Clark and S.A. Johnson, Private Communication.

2. Stanton Redcroft, TG750, Information Sheet.

3. N.B. Colthup, L.H. Daly, and S.E. Wiberley, "Introduction to I.R. and Raman Spectroscopy", 2nd Ed. Academic Press, 1975.

COLLOQUIA AND CONFERENCES

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing:

(A) all research colloquia, research seminars and lectures arranged by the Department of Chemistry during the period of the author's residence as a postgraduate student;

(B) all research conferences attended and papers presented by the author during the period when research for the thesis was carried out;

(C) details of the postgraduate induction course.

* denotes lectures attended.

(A) RESEARCH COLLOQUIA, SEMINARS AND LECTURES

1. Durham University Chemistry Department Colloquia.

1981

* 14 October — Prof. E. Kluk (Katowice): "Chemoluminescence and photo-oxidation".

* 28 October — Dr. R.J.H. Clark (U.C.L.): "Resonance Raman Spectroscopy".

* 6 November — Dr. W. Moddeman (Monsanto): "High energy materials".

* 18 November — Prof. M.J. Perkins (London): "Spin-trapping and and nitroxide radicals".

* 25 November — Dr. M. Baird (Newcastle): "Intramolecular reactions of carbenes and carbenoids".

* 2 December — Dr. G. Beamson (Durham): "Photoelectron spectroscopy in a strong magnetic field".

1982

20 January — Dr. M.R. Bryce (University of Durham), "Organic metals".

27 January — Dr. D.L.H. Williams (University of Durham), "Nitrosation and nitrosoamines".

* 3 February — Dr. D. Parker (University of Durham), "Modern methods of determining enantiomeric purity".

* 10 February — Dr. D. Pethrick (University of Strathclyde), "Conformation of small and large molecules".

* 17 February — Prof. D.T. Clark (University of Durham), "Plasma Polymerization".

24 February — Prof. R.D. Chambers (University of Durham), "Recent reactions of fluorinated internal olefins".

* 2 March — Dr. L. Field (University of Oxford), "Applications of N.M.R. to biosynthetic studies on penicillin".

* 3 March — Dr. P. Bamfield (I.C.I. Organics Division), "Computer aided design in synthetic organic chemistry".

* 17 March — Prof. R.J. Haines (University of Natal), "Clustering around Ruthenium, Iron and Rhodium".

* 7 April — Dr. A. Pensak (DuPont, U.S.A.), "Computer aided synthesis".

* 5 May — Dr. G. Tennant (University of Edinburgh), "Exploitation of the aromatic nitro-group in the design of new heterocyclisation reactions".

* 7 May — Dr. C.D. Garner (University of Manchester), "The structure and function of Molybdenum centres in enzymes".

* 26 May — Dr. A. Welch, (University of Edinburgh), "Conformation patterns and distortion in carbometalloboranes".

* 14 June — Prof. C.M.J. Stirling (University College of Wales, Bangor), " How much does strain affect reactivity?".

* 28 June — Prof. D.J. Burton (University of Iowa, U.S.A.), "Some aspects of the chemistry of fluorinated phosphonium salts and their phosphonates".

* 2 July — Prof. H.F. Koch (Ithaca College, University of Cornell, U.S.A.), "Proton transfer to and elimination reactions from localized and declocalized carbanions".

* 13 September — Prof. R. Neidlein (University of Heidelberg, FRG), "New aspects and results of bridged annulene chemistry".

* 27 September — Dr. W.K. Ford (Xerox Research Center, Webster, N.Y.), "The dependence of the electron structure of polymers on their molecular architecture".

* 13 October — Dr. W.J. Feast (University of Durham), "Approaches to the synthesis of conjugated polymers".

* 14 October — Prof. H. Suhr (University of Tubingen, FRG), "Preparative Chemistry in Non-equilibrium plasmas".

* 27 October — Dr. C.E. Housecroft (Oxford High School/Notre Dame University", "Bonding capabilities of butterfly-shaped Fe_4 units implications for C-H bond activation in hydrocarbon complexes".

* 28 October — Prof. M.F. Lappert, F.R.S., (University of Sussex), "Approaches to asymmetric synthesis and catalyses using electron-rich olefins and some of their metal complexes".

* 15 November — Dr. G. Bertrand (University of Toulouse, France), "Crutius rearrangement in organometallic series. A route for hybridised species".

* 24 November — Prof. G.G. Roberts (Applied Physics, University of Durham), "Langmuir-Blodgett films: Solid state polymerisation of diacetylenes".

2 December — Dr. G.M. Brook (University of Durham), "The fate of the ortho-fluorine in 3,3-sigmatropic reactions involving polyfluoroaryl and -heteroaryl systems".

* 8 December — Dr. G. Wooley (Trent Polytechnic), "Bonds in transition metal-cluster compounds".

1983

* 12 January — Dr. D.C. Sherrington (University of Strathclyde), "Polymer-supported phase transfer catalysts".

* 9 February — Dr. P. Moore (University of Warwick), "Mechanistic studies in solution by stopped flow F.T.-N.M.R. and high pressure NMR line broadening".

* 21 February — Dr. R. Lynder-Bell (University of Cambridge), "Molecular motion in the cubic phase of NaCN".

*2 March — Dr. D. Bloor (Queen Mary College, University of London), "The solid-state chemistry of diacetylene monomers and polymers".

*8 March — Prof. D.C. Bradley, F.R.S. (Queen Mary College, University of London), "Recent developments in organo-imido-transition metal chemistry".

*9 March — Dr. D.M.J. Lilley (University of Dundee), "DNA, Sequence, Symmetry, Structure and supercooling".

11 March — Prof. H.G. Viehe (University of Louvain, Belgium), "Oxidations on Sulphur", "Fluorine substitutions in radicals".
[The W.K.R. Musgrave Lecture].

*16 March — Dr. I. Gosney (University of Edinburgh), "New extrustion reactions: Organic synthesis in a hot-tube

*25 March — Prof. F.G. Baglin (University of Nevada, U.S.A.), "Interaction induced Raman spectroscopy in supra-critical ethane".

*21 April — Prof. J. Passmore (University of New Brunswick,U.S.A "Novel selenium-iodine cations".

*4 May — Prof. P.H. Plesh (University of Keele), "Binary ionisation equilibria between two ions and two molecules. What Ostwald never thought of".

*10 May — Prof. K. Burger (Technical University of Munich,FRG) "New reaction pathways from trifluoromethyl-substituted heterodienes to partially fluorinated heterocyclic compounds".

11 May — Dr. N. Isaacs (University of Reading), The Application of high pressures to the theory and practice of organic chemistry".

*13 May — Dr. R. de Koch (Caloin College, Grand Rapids, Michigan/Free University, Amsterdam) "Electronic structural calculations in organometallic cobalt cluster molecules. Implications for metal surfaces".

*16 May — Prof. R.J. Lagow (University of Texas, U.S.A.), "The chemistry of polylithium organic compounds. An unusual class of matter".

*18 May — Dr. D.M. Adams (University of Leicester), "Spectroscopy at very high pressures".

*25 May — Dr. J.M. Vernon (University of York), "New heterocyclic chemistry involving lead tetraacetate".

15 June — Dr. A. Pietrzykowski (Technical University of Warsaw/University of Strathclude), "Synthesis, structure and properties of Aluminoxanes".

*22 June — Dr. D.W.H. Rankin (University of Edinburgh), "Floppy molecules - the influence of phase on structure".

*5 July — Prof. J. Miller (University of Camfinas, Brazil), "Reactivity in nucleophilic substitution reactions".

*5 October — Prof. J.P. Maier (University of Basel, Switzerland), "Recent approaches to spectroscopic characterization of cations".

*12 October — Dr. C.W. McLeland (University of Port Elizabeth, Australia), Cyclization of aryl alcohols through the intermediacy of alkoxy radicals and aryl radical cations".

*19 October — Dr. N.W. Alcock (University of Warwick), "Aryl tellurium (IV) compounds, patterns of primary and secondary bonding".

*26 October — Dr. R.H. Friend (Cavendish Laboratory, University of Cambridge), "Electronic properties of conjugated polymrs".

30 November — Prof. I. Cowie (University of Stirling), "Molecular interpretation of non-relaxation processes in polymer glasses".

*14 December — Prof. R.J. Donovan (University of Edinburgh), "Chemical and physical processes involving the ion-pair states of the halogen molecules".

1984

*10 January — Prof. R. Hester (University of York), "Nanosecond laser spectroscopy of reaction intermediates".

*18 January — Prof. R.K. Harris (University of East Anglia), Multi-nuclear solid state magnetic resonance".

*8 February — Dr. B.T. Heaton (University of Kent), "Multi-nuclear n.m.r. studies".

*15 February — Dr. R.M. Paton (University of Edinburgh), "Heterocyclic syntheses using nitrile sulphides".

*7 March — Dr. R.T. Walker (University of Birmingham), "Synthesis and biological properties of some 5-substituted uracil derivatives; yet another example of serendipity in antiviral chemotherapy".

*21 March — Dr. P. Sherwood (University of Newcastle), "X-ray photoelectron spectroscopic studies of electrode and other surfaces".

*23 March — (Informal colloquium) Dr. A. Ceulemans (Catholic University of Leuven), "The Development of Field-Type Models of the Bonding in Molecular Clusters".

2 April — Professor K. O'Driscoll (University of Waterloo), "Chain Ending Reactions in Free Radical Polymerisation

3 April — Professor C.H. Rochester (University of Dundee), "Infrared Studies of Adsorption at the Solid-Liquid Interface".

25 April — Dr. R.M. Acheson (Department of Biochemistry, University of Oxford), "Some Heterocyclic Detective Stories".

*27 April — Dr. T. Albright (University of Houston), "Sigmatropic Rearrangements in Organometallic Chemistry".

*14 May — Professor W.R. Dolbier, Jr., (University of Florida) "Cycloaddition Reactions of Fluorinated Allenes".

16 May — Dr. P.J. Garratt (University College, London), "Syntheses with Dilithiated Vicinal Diesters and Carboximides".

31 May — Dr. A. Haaland (University of Oslo), "Electron Diffraction Studies of some Organometallic Compounds"

*11 June — Dr. G.B. Street (I.B.M. San José), "Conducting Polymers derived from Pyrroles".

2. DURHAM UNIVERSITY CHEMICAL SOCIETY LECTURES

1981

*22 October — Dr. P.J. Corish (Dunlop): "What would life be like without rubber".

*29 October — Miss J.M. Cronyn (Durham): "Chemistry in Archaeology".

*12 November — Prof. A.I. Scott (Edinburgh): "An organic chemist's view of life through the n.m.r. tube".

*19 November — Prof. B.L. Shaw (Leeds): "Big rings and metal-carbon bond formation".

*3 December — Dr. W.O. Ord (Northumbria Water Authority): "The rôle of the scientist in a regional water authority

1982

*28 January — Prof. I. Fells (University of Newcastle upon Tyne), "Balancing the Energy Equations".

* 11 February — Dr. D.W. Turner (University of Oxford), "Photoelectrons in a Strong Magnetic Field".

* 18 February — Prof. R.K. Harris (University of East Anglia), "N.m.r. in the 1980s".

* 25 February — Prof. R.O.C. Norman, F.R.S. (University of York), "Turning Points and Challenges for the Organic Chemist".

* 4 March — Dr. R. Whyman (I.C.I. Ltd., Runcorn), "Making Metal Clusters Work".

* 14 October — Mr. F. Shenton (County Analyst, Durham), "There is death in the pot".

* 28 October — Prof. M.F. Lappert, F.R.S. (University of Sussex), "The Chemistry of Some Unusual Subvalent Compounds of the Main Group IV and V Elements".

* 4 November — Dr. D.H. Williams (University of Cambridge), Studies on the Structures and Modes of Action of Antibiotics".

* 11 November — Dr. J. Cramp (I.C.I. Ltd.), "Lasers in Industry".

* 25 November — Dr. D.H. Richards, P.E.R.M.E. (Ministry of Defence) "Terminally Functional Polymers, their Synthesis and Uses".

1983

* 27 January — Prof. D.W.A. Sharp (University of Glasgow), "Some Redox Reactions in Fluorine Chemistry".

* 3 February — Dr. R. Manning (Department of Zoology, University of Durham), "Molecular Mechanisms of Hormone Action

* 10 February — Sir Geoffrey Allen, F.R.S. (Unilever Ltd.), "U.K. Research Ltd.".

* 17 February — [R.S.C. Centenary Lecture], Prof. A.G. MacDiarmid, (University of Pennsylvania),"Metallic Covalent Polymers: $(SN)_x$ and $(CH)_x$ and their derivatives".

*3 March — Prof. A.C.T. North (University of Leeds), "The Use of a Computer Display System in Studying Molecular Structures and Interactions".

*20 October — Prof. R.B. Cundall (University of Salford), "Explosives".

*3 November — Dr. G. Richards (University of Oxford), "Quantum pharmacology".

10 November — Dr. J. Harrison (Sterling Organic), "Applied Chemistry and the Pharmaceutical Industry".

24 November — Prof. D.A. King (University of Liverpool), "Chemistry in two dimensions".

1 December — Dr. J.D. Coyle (The Open University), "The problem with sunshine".

1984

26 January — Prof. T.L. Blundell (Birkbeck College, London), "Biological recognition: Interactions of macromolecular surfaces".

2 February — Prof. N.B.H. Jonathan (University of Southampton), "Photoelectron spectroscopy - a radical approach".

16 February — Prof. D. Phillips (The Royal Institution), "Luminescence and photochemistry - a light entertainmentP.

*23 February — Prof. F.G.A. Stone, F.R.S. (University of Bristol), "The use of carbene and carbyne groups to synthesise metal clusters".
[The Waddington Memorial Lecture].

*1 March — Prof. A.J. Leadbetter (Rutherford Appleton Labs.), "Liquid Crystals".

8 March — Prof. D. Chapman (Royal Free Hospital School of Medicine, University of London), "Phospholipids and biomembranes: basic structure and future techniques

28 March (R.S.C. Centenary Lecture]

Prof. H. Schmidbaur (Technical University of Munich, FRG), "Ylides in coordination sphere of metals: synthetic, structural and theoretical aspects".

(B) RESEARCH CONFERENCES ATTENDED

Achema '82; International Meeting on Chemical Engineering, 20th Exhibition - Congress. Frankfurt-am-Main,9-15 June,1982

Graduate Symposium, Durham, April 1982.

Scottish Dalton Meeting, Heriot-Watt University, February 1983.

Graduate Symposium, Durham, April 1983.

Scottish Dalton Meeting, Glasgow University, February 1984.

Graduate Symposium, Durham, April 1984.

Second International Converence on the Chemistry of the Platinum Group Metals, University of Edinburgh,1-6 July 1984.

A poster was presented by the author entitled - "Amidino - complexes of the Nickel Group Metals".

(C) POSTGRADUATE INDUCTION COURSE

In each part of the course, the uses and limitations of the various services available were explained.

Departmental Organisation - Dr. E.J.F. Ross.

Electrical appliances and infrared spectroscopy - Mr.R.N.Brown.

Chromotography - Mr. J.A. Parkinson.

Microanalysis - Mr. T.F. Holmes and Mrs. M. Cocks.

Atomic absorption spectrometry and inorganic analysis - Mr. R. Coult.

Mass spectroscopy - Dr. M. Jones.

N.m.r. spectroscopy - Dr. R.S. Matthews.

Glassblowing techniques - Mr. R. Hart and Mr. G. Haswell.

Safety matters - Dr. M.R. Crampton.